

PATENT ABSTRACTS OF JAPAN

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(71)Applicant : KONICA CORP

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(54) INK JET RECORDING PAPER

(57)Abstract:

PROBLEM TO BE SOLVED: To maintain high ink absorption while showing high luster, and form/ record a high grade image with outstanding water resistance, moisture resistance and light resistance, in printing an image with a water ink.

SOLUTION: This ink jet recording paper has a support and at least, two ink receptive layers formed on the support. In this case, the ink receptive layer contains a silica fine particle with an average primary particle diameter of 20nm or less and a hydrophilic binder, and at least, the remotest layer from the support on the ink receptive layer side contains a water-soluble cationic polymer.

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CLAIMS

[Claim(s)]

[Claim 1] the ink jet record form which has at least the two-layer ink absorbing layer prepared a base material and on it — setting — this ink absorbing layer — an average of 1 — the ink jet record form characterized by containing a water-soluble cationic polymer in the layer which contained the silica system particle and the hydrophilic binder not more than order particle diameter 20nm, and is most separated from the base material by the side of an ink absorbing layer at least.

[Claim 2] The ink jet record form according to claim 1 characterized by being at least one as which said hydrophilic binder is chosen from polyvinyl alcohol and its derivative.

[Claim 3] The ink jet record form according to claim 1 or 2 characterized by said water-soluble cationic polymer and hydrophilic binder being 0.3:1-3:1 in a weight ratio.

[Claim 4] The ink jet record form of claim 1-3 characterized by all ink absorbing layers containing said water-soluble cationic polymer given in any 1 term.

[Claim 5] The ink jet record form of claim 1-4 characterized by containing at least one sort chosen from the compound which absorbs an image stabilizer and ultraviolet rays as a fading inhibitor given in any 1 term.

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the ink jet record form which has improved glossiness, ink absorptivity, a water resisting property, moisture resistance, and lightfastness in detail about the ink jet record form which records using water color ink.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the ink jet record form which has improved glossiness, ink absorptivity, a water resisting property, moisture resistance, and lightfastness in detail about the ink jet record form which records using water color ink.

[0002]

[Description of the Prior Art] although ink jet record makes the minute drop of ink fly by various working principles, and is made to adhere to record sheets, such as paper, and an image, an alphabetic character, etc. are recorded, a high speed, the low noise, and multiple-color-izing are comparatively easy — etc. — it has the advantage. About the blinding of a nozzle and the maintenance which had become a problem from the former by this method, from both sides of ink and equipment, amelioration progresses and it has spread through various fields, such as various printers, facsimile, and a computer terminal, quickly in current.

[0003] As a record form used by this ink jet recording method, also when a printing dot laps [that a color tone is brightly skillful and absorption of ink] early, the diffusion to the longitudinal direction of ink flowing out or not spreading and a printing dot is not large [the concentration of a printing dot is high, and] beyond the need, and it is required that the circumference should be smooth and should not fade etc.

[0004] Since it becomes nonuniformity, and the color of each other in the border area of a color which a drop causes a HAJIKI phenomenon on a record form, and is different spreads and it is easy to reduce image quality greatly in case the liquid ink drop of two or more colors laps and is recorded, when especially ink rate of absorption is slow, it is required to give ink absorptivity high as a record form.

[0005] In order to solve these problems, very many techniques are proposed from the former.

[0006] As the pigment in the record form which carried out humidity of the coating for surface treatment to the low size stencil paper indicated by JP,52-53012,A, the record form which prepared the coated layer of ink absorptivity in the support surface indicated by JP,55-5830,A, and ****-ed indicated by JP,56-157,A The record form containing non-colloid silica powder, the record form which used together the inorganic pigment indicated by JP,57-107878,A and the organic pigment, The record form which has two hole distribution peaks indicated by JP,58-110287,A, The record form which consists of a vertical two-layer porous layer indicated by JP,62-111782,A, The record form which has the indeterminate form crack indicated by JP,59-68292,A, 59-123696, the 60-18383 official report, etc., The record form which has the impalpable powder layer indicated by JP,61-135786,A, 61-148092, the 62-149475 official report, etc., JP,63-252779,A, JP,1-108083,A, 2-136279, The record form containing the pigment which has the specific physical-properties value indicated by 3-65376, 3-27976, etc., or a particle silica, JP,57-14091,A, 60-219083, 60-210984, 61-20797, 61-188183, JP,5-278324,A, 6-92011, 6-183134, 7-137431, The record form containing particle silicas, such as a colloid silica indicated by 7-276789 etc., And JP,2-276671,A, 3-67684, 3-215082, A large number are known for the record form containing the hydrated alumina particle indicated by 3-251488, 4-67986, 4-263983, the 5-16517 official report, etc.

[0007] However, since many ink absorbing layers with many openings will have irregularity with micro interface with air and coat front face, the incident light to an ink absorbing layer is scattered about or transparency is barred when an ink absorbing layer absorbs ink or it consists of only layers which have many openings for holding, it becomes or tends to be hard to come out opaquely lusterless.

[0008] Moreover, in order to form an opening, there is a fault out of which the smooth nature on the front face of a coat by own irregularity of a pigment or the irregularity of the secondary floc of a pigment falls, and gloss cannot come easily.

[0009] On the other hand, many ink jet record forms of the type which absorbs ink and is held in a swelling operation of the binder of an ink absorption layer are also known, without preparing an opening into a coat.

[0010] For example, many the recording papers, films, etc. which applied hydrophilic binders, such as gelatin, casein, starch, an alginic acid, polyvinyl alcohol, various kinds of denaturation polyvinyl alcohol, a polyvinyl pyrrolidone, polyethylene oxide, polypropylene oxide, a carboxymethyl cellulose, HIDOROKI ethyl cellulose, a dextran, and a pullulan, on the base material as binders are known from the former.

[0011] Although these record forms are inferior in ink absorptivity compared with the record form which has the above-mentioned opening, high glossiness and optical density, and a clear image are obtained, and they are useful as a high-definition record application.

[0012] since it differed in the color printing paper in which a coloring matter molecule be distribute in the state of a high-concentration particle in oils and a coloring matter molecule existed between the inside of a binder , and an opening independently , a fault which waterdrop be pour on a recording surface , or spread when it be save under high humidity conditions the printing back for a long period of time , or be easy flow out be in various kinds of ink jet record forms suitable for the water-soluble above-mentioned ink .

[0013] In order to improve the water resisting property and moisture resistance of this coloring matter, the various methods of making coloring matter fix in a binder from the former are proposed. Especially an effective means is the approach of adding as a particle latex by using as a uniform water solution the polymer which has the nitrogen atom of the 3rd class or the 4th class.

[0014] For example, the ink jet record form applied on stencil paper or a polyethylene terephthalate film base material by using as an ink absorbing layer the coating liquid which uses gelatin as some binders at JP,57-36692,A, and contains a basic mordant is indicated.

[0015] The water-color-ink record form which infiltrated polyethyleneimine into paper is indicated by JP,53-49113,A.

[0016] The record material which has the electrolyte polymer which has a cation or an anion radical is indicated by JP,58-24492,A.

[0017] The 1st class thru/or tertiary amine, or quarternary ammonium salt is contained in an ink absorbing layer, and the charge of a recorded material which has pH of an ink maintenance layer in 2-8 is indicated by JP,63-224988,A.

[0018] The ink jet record form which has a layer containing the polymer which has the hydrophilic polymer mordant which has the 3rd class or the 4th class nitrogen atom, and a hydrophilic radical is indicated by JP,63-307979,A.

[0019] The record ingredient which made the organic base of polyethyleneimine contain in the coating layer in a base material or on a base material is indicated by JP,59-198186,A and 59-198188.

[0020] The ink jet record approach using the ink containing a specific color and the record ingredient containing polyamine etc. is indicated by JP,60-46288,A.

[0021] The ink jet record form containing the poly allylamine is indicated by JP,61-61887,A, 61-72581, 61-252189, and 62-174184.

[0022] The ink jet record ingredient containing the polymer which has an intermolecular hydrogen bridge, and the polymers (a polyethylene glycol, polyvinyl pyrrolidone, etc.) which do not have a hydrogen bond nature machine among molecules (gelatin, polyethylene RENIMIN, etc.) is indicated by JP,61-172786,A.

[0023] The ink jet record form which applies or infiltrated the cationic polymer and the cationic surface active agent on the base material is indicated by JP,63-162275,A.

[0024] The record form which superimposed the color fixing layer which uses a quarternary-ammonium-salt polymerization object and cation denaturation polyvinyl alcohol as a principal component on a plastics base material, and the color transparency and ink absorption layer which were prepared on it on JP,6-143798,A is indicated.

[0025] Furthermore, JP,59-20696,A, 59-33176, 59-33177, 59-96987, 59-155088, 60-11389, 60-49990, 60-83882, 60-109894, 61-277484, 61-293886, 62-19483, 62-198493, 63-49478, 63-115780, 63-203896, 63-274583, 63-280681, The nitrogen atom of the 3rd class or the 4th class of specification [63-260477, JP,1-9776,A, 1-20188, 1-24784, 1-40371, 3-133686, 6-234268, and 7-125411] respectively Adding the polymer or compound to contain all over an ink absorbing layer is indicated.

[0026] However, although the water resisting property of coloring matter improves according to the above-mentioned conventional approach, that to which lightfastness falls is most.

[0027] Moreover, a polymer of a certain kind had the fault that cost was high, and had the fault of spreading with it not being performed, or being unable to carry out little deer use. [low compatibility with the binder to be used and] [good]

[0028] Although the record sheet which makes the deck-watertight-luminaire-ized agent of a coat exist in the ink absorption layer which becomes JP,7-125412,A from a binder and a filler, and carries out localization of the fixing agent of an ink color into the front face of this ink absorption layer and/or a surface, and its manufacture approach were indicated, it is characterized by to carry out the overcoat of the color fixing agent which cannot be added in an ink absorption layer to an absorption layer, and there was a fault with the high cost by letting a spreading process pass twice.

[0029] Although the record form with which a laminating and JP,7-242056,A prepare an ink absorption layer in JP,5-124329,A at the color fixing layer which uses a quarternary-ammonium-salt polymerization object as a principal component for the anionic layer of a pigment and a water-soluble binder layer at JP,5-131742,A, and

prepare the water meltable alcoholic insoluble polymer content layer of a silica particle and the amount of specification one by one on a cationic polymer layer at a quarternary-ammonium-salt water solubility polymer content absorption layer was indicated, ink absorptivity and a coloring matter water resisting property were able to say that neither was enough.

[0030]

[Problem(s) to be Solved by the Invention] This invention is offering the ink jet record form which can carry out formation record of the high-definition image which is made in view of the above-mentioned actual condition, and the purpose of this invention moreover has high ink absorptivity, maintaining high glossiness in printing by water color ink, and was excellent in a water resisting property, moisture resistance, and lightfastness.

[0031]

[Means for Solving the Problem] The above-mentioned purpose of this invention is attained by the following configuration.

[0032] (1) the ink jet record form which has at least the two-layer ink absorbing layer prepared a base material and on it — setting — this ink absorbing layer — an average of 1 — the ink jet record form characterized by containing a water-soluble cationic polymer in the layer which contained the silica system particle and the hydrophilic binder not more than order particle diameter 20nm, and is most separated from the base material by the side of an ink absorbing layer at least.

[0033] (2) The ink jet record form given in (1) characterized by being at least one as which said hydrophilic binder is chosen from polyvinyl alcohol and its derivative.

[0034] (3) (1) characterized by said water-soluble cationic polymer and hydrophilic binder being 0.3:1–3:1 in a weight ratio, or an ink jet record form given in (2).

[0035] (4) The ink jet record form of (1) – (3) characterized by all ink absorbing layers containing said water-soluble cationic polymer given in any 1 term.

[0036] (5) The ink jet record form of (1) – (4) characterized by containing at least one sort chosen from the compound which absorbs an image stabilizer and ultraviolet rays as a fading inhibitor given in any 1 term.

[0037] Hereafter, this invention is explained to a detail.

[0038] High ink absorptivity is acquired by the opening in which the ink jet record form of this invention is formed of the binder and silica system particle of a hydrophilic property.

[0039] Generally as the formation approach of a typical opening with a solid-state particle and a hydrophilic binder, the following approaches can be considered.

[0040] (1) Apply the coating liquid containing a porosity solid-state particle and a hydrophilic binder on a base material. As opposed to the approach (2) hydrophilic-property binder which forms an opening between the inside of a porosity particle, or a particle The coating liquid containing the solid-state particle which has the volume more than equivalence (preferably 10 or more times) in general, and a hydrophilic binder is applied on a base material. Between solid-state particles The approach the approach (3) mean particle diameter which creates an opening makes solid-state particle about 0.1 micrometers or less condense at the time of coating liquid preparation or coat formation, forms a secondary particle or the three-dimensional structure, and creates an opening.

[0041] Although the approach (1) was generally excellent in ink absorptivity and it was widely used by coat paper etc. from before, the porosity solid-state particle was a particle with the big particle diameter of the micron order which the secondary most is condensing so that it might be represented by the synthetic indeterminate form silica, and was difficult to acquire glossiness sufficient in just the opening layer obtained by this approach.

[0042] Although excelled in ink absorptivity, since a solid-state particle was a high ratio to a hydrophilic binder, when the embrittlement of a coat was not avoided but unabsorbent base materials, such as plastic film, were used especially, various problems, such as a crack of an absorption layer and powder omission, might arise said approach (2) at the time of a manufacture process or use.

[0043] In this invention, a desirable mode is said approach (3). This approach is the approach of forming a flocculation condition by the solid-state particle, and forming the network structure into a coat, and into the water solution which contains a hydrophilic polymer preferably, the primary ultrafine particle in a distributed condition is formed via the condition of condensing each other, where a point of contact is restricted comparatively. that such a flocculation condition is linear or the condition that what formed floc in the shape of branching was distributed in the water solution — or the condition of such flocs condensing each other further and taking the three-dimension network structure in a water solution is included. Even if it is which case, detailed structure can be formed into the formed coat by carrying out spreading desiccation of this water solution on a base material.

[0044] Thus, in general, from the magnitude of a primary particle, the magnitude of the detailed opening in the obtained coat is about several times those magnitude of this, and has the description which is the opening of detailed magnitude.

[0045] It is formed in the water solution which has the approach of being hard to condense a primary particle to

each other, carrying out ultralow volume addition of the hydrophilic polymer which accelerates condensation of a particle in the water solution containing the hydrophilic polymer which can exist in stability as an approach of forming such a flocculation condition, for example, and forming condensation slightly, or the water-soluble polymer which can perform a primary particle front face and weak coupling.

[0046] Especially in this invention, it is desirable from that the latter approach tends to form the amount of an opening in stability that it is comparatively easy to control, and more amounts of openings being obtained as compared with the amount of the particle to be used, and since a coat with the still higher glossiness of a coat is obtained, the particle diameter (first [an average of] particle diameter) of a primary particle uses a silica particle 20nm or less.

[0047] As a hydrophilic binder used for the ink jet record form of this invention Gelatin or a gelatin derivative, a polyvinyl pyrrolidone (about 200,000 or more have desirable average molecular weight), A pullulan, polyvinyl alcohol, or its derivative (about 20,000 or more have desirable average molecular weight), A polyethylene glycol (100,000 or more have a desirable mean molecular weight), a carboxymethyl cellulose, Hydroxyethyl cellulose, a dextran, a dextrin, polyacrylic acid, and its salt, An acrylamide system polymer, an agar, a kappa carrageenan, lambda-carrageenan, iota-carrageenan, xanthene gum, locust bean gum, an alginic acid, A polyalkylene oxide system copolymerization nature polymer given in gum arabic, a pullulan, JP,7-195826,A, and 7-9757, a water-soluble polyvinyl butyral, Or polymers, such as independent or a copolymer which repeats and has these vinyl monomers of the vinyl monomer which has the carboxyl group and sulfonic group of a publication, can be mentioned to JP,62-245260,A. These hydrophilic binders may be used independently and may use two or more sorts together.

[0048] In the ink jet record form of this invention, the case where primary [an average of] particle diameter uses polyvinyl alcohol or denaturation polyvinyl alcohol as a hydrophilic binder to a silica particle as a particle 20nm or less is desirable. In this case, hydrogen bond with weak silanol group of a particle silica front face and hydroxyl group of vinyl alcohol is performed, and said flocculation object is formed good.

[0049] Especially as said silica particle, a 6-15nm thing is the most desirable. Moreover, as a secondary particle which these connected, it is desirable to make it preferably set to about 30-100nm 20-200nm.

[0050] The particle silica compounded by the synthetic approach by which such a particle silica is called a usual gaseous-phase method given [for example,] in JP,60-204390,A is used preferably. Moreover, this silica particle may be the object which cation denaturation could be made [which was] like a silane coupling agent in the front face, and was processed by aluminum, calcium, Mg, Ba, etc.

[0051] The hydrophilic binder preferably used by this invention is polyvinyl alcohol or its derivative. Polyvinyl alcohol or its derivative is the polyvinyl alcohol or cation denaturation polyvinyl alcohol of completeness or partial saponification. one especially desirable also in polyvinyl alcohol — whenever [saponification] — 80 or more parts — or full saponification is carried out. moreover, the viewpoint which improves coat brittleness to average degree of polymerization — 500-3500 — the thing of 1000-3500 is used especially preferably.

[0052] Moreover, it is polyvinyl alcohol which has the 1-3rd class amino group which is indicated by JP,61-10483,A, for example, and the 4th class ammonium in the principal chain of the above-mentioned polyvinyl alcohol, or a side chain as cation denaturation polyvinyl alcohol.

[0053] By this approach, as a hydrophilic binder, it is desirable in order for 1500 or more to carry out especially polymerization degree especially of the polyvinyl alcohol used preferably for not causing a crack to a coat 1000 or more.

[0054] Here, the ratios of polyvinyl alcohol and the above-mentioned silica are 1:10-1:1 in general, and the range of them is 1:7-1:2 preferably.

[0055] It explains briefly [below] about the approach of forming the coat which contains a flocculation object using polyvinyl alcohol and a particle silica.

[0056] In the polyvinyl alcohol water solution (in general 5 - 15%) which maintained pH at 6-8, and the temperature of about 40 degrees C, it adds gradually, strong-agitating silica dispersion liquid (in general 5 - 15%), and an ultrasonic disperser, a high-speed homogenizer, etc. distribute after addition termination. In this case, in order to prepare uniform coating liquid, water miscibility organic solvents, such as various kinds of surfactants, and a methanol, an acetone, may be used if needed. Subsequently, after adding various kinds of additives, it adjusts to target viscosity required for spreading, and the coat which has the above-mentioned opening by applying and drying by the well-known approach on a base material is obtained.

[0057] Although other hydrophilic binders can be made to contain in said opening layer, as for those hydrophilic binders, it is preferably desirable that it is 20 or less % of the weight in general to said polyvinyl alcohol or its derivative.

[0058] A well-known solid-state particle inorganic [various kinds of] or organic can be conventionally used for the ink absorption layer of the ink jet record form of this invention in an ink jet record form as a solid-state particle in the range which does not spoil the effectiveness of this invention. As an example of the non-subtlety particle used, white inorganic pigments, such as precipitated calcium carbonate, whiting, a magnesium carbonate,

a kaolin, clay, talc, a calcium sulfate, a barium sulfate, a titanium dioxide, a zinc oxide, zinc hydroxide, zinc sulfide, zinc carbonate, a hydrotalcite, aluminum silicate, the diatom earth, a calcium silicate, a magnesium silicate, synthetic amorphous silica, a gaseous-phase method silica, colloidal silica, an alumina, a colloidal alumina, pseudo-boehmite, an aluminum hydroxide, a lithopone, a zeolite, and a magnesium hydroxide etc. can be mentioned

[0059] On the other hand as an example of an organic particle, polystyrene, polyacrylic ester, polymethacrylic acid ester, polyacrylamides, polyethylene, polypropylene, a polyvinyl chloride, polyvinylidene chlorides or these copolymers, a urea-resin, or melamine resin is mentioned.

[0060] The water-soluble cationic polymer for improving the absorptivity of ink, the water resisting property of coloring matter, and damp-proof both in the ink jet record form of this invention is used.

[0061] For example, the absorptivity of ink may be spoiled by the approach of adding the particle latex of the polymer which has a nitrogen atom of the 3rd class or the 4th class like a JP,57-36692,A publication, and it is not desirable. Although a reason is not clear, probably it is presumed for a latex particle to bar the opening formation by the hydrophilic binder and the silica system particle. As a water-soluble cation polymer used for this invention Polyethyleneimine, JP,59-20696,A, 59-33176, 59-33177, 59-155088, 60-11389, 60-49990, 60-83882, 60-109894, 62-198493, 63-49478, 63-115780, The polymer which has the 1-3rd class amino group indicated by 63-280681, JP,1-40371,A, 6-234268, 7-125411, etc. and a quarternary-ammonium-salt radical is used preferably.

[0062] Among these especially the water-soluble polymer used preferably is expressed with the following general formula.

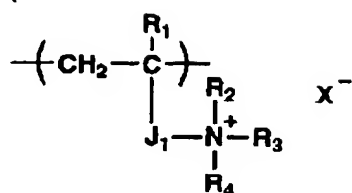
[0063] General formula (L)

(A) A is expressed with following general formula (A-1) - (A-8) among an X-(B) Y-(C) Z general formula (L).

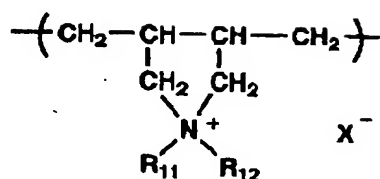
[0064]

[Formula 1]

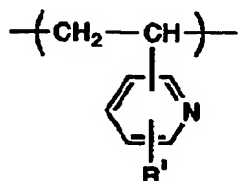
一般式(A-1)



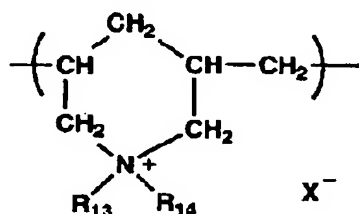
一般式(A-6)



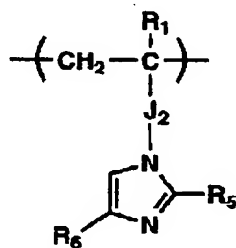
一般式(A-2)



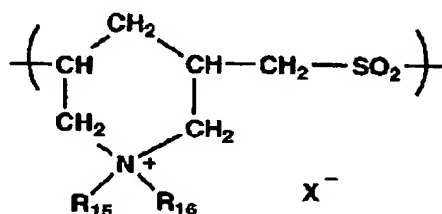
一般式(A-7)



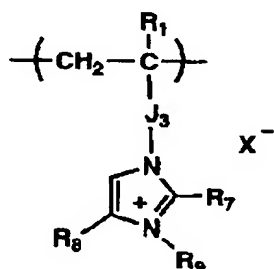
一般式(A-3)



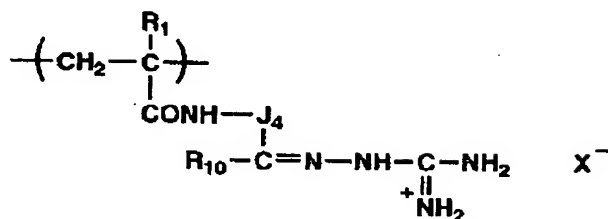
一般式(A-8)



一般式(A-4)



一般式(A-5)



[0065] In a general formula (A-1), R1 expresses the alkyl group of a hydrogen atom or the carbon atomic numbers 1-4. J1 expresses a divalent connection radical and expresses the benzyl which is not permuted [a methylene group, a permutation, or] or -COY-. A carbon atom is the divalent connection radical of 1-20, for example, Y expresses an alkylene group, an arylene radical, and a -O-Y'- radical and -NH-Y'-radical (Y' is an alkylene group, an arylene radical, an aralkylene group, etc.). R2 may express the alkyl group of a hydrogen atom or the carbon atomic numbers 1-18, or the aralkyl radical of the carbon atomic numbers 7-18, and these alkyl groups or an aralkyl radical may have a substituent. R3 and R4 may express the alkyl group of the carbon atomic numbers 1-18, or the aralkyl radical of the carbon atomic numbers 7-18 respectively, and these alkyl groups or an aralkyl radical may have a substituent. X- expresses an anion, for example, expresses halogen ion, alkyl sulfonic-acid ion, aryl sulfonic-acid ion, acetic-acid ion, etc.

[0066] In a general formula (A-2), R' expresses the alkyl group of a hydrogen atom or the carbon atomic numbers 1-18, or the aralkyl radical of the carbon atomic numbers 7-18.

[0067] a general formula (A-3) — and (A-4) it sets and J2 and J3 express a mere joint hand or divalent connection radicals (an alkylene group, an arylene radical, aralkylene group, etc.). R1 and X- are synonymous

with R1 of a general formula (A-1), and X-. R5-R8 express a hydrogen atom, an alkyl group, or an aralkyl radical independently, respectively. R9 expresses an alkyl group or an aralkyl radical.

[0068] In a general formula (A-5), R1 and X- are synonymous with R1 of a general formula (A-1), and X-. R10 expresses an alkyl group.

[0069] In a general formula (A-6), (A-7), and (A-8), R11, R12, R13, R14, R15, and R16 may express the alkyl group of a hydrogen atom or the carbon atomic numbers 1-18, or the aralkyl radical of the carbon atomic numbers 7-18 independently, respectively, and these alkyl groups or an aralkyl radical may have the substituent. X- is synonymous with X- of a general formula (A-1).

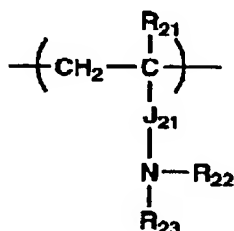
[0070] A general formula (A-1) is used especially more preferably still also in this.

[0071] (B) expresses the repeat unit guided from the monomer chosen from the following general formula (B-1) and acrylamide, methacrylamide, N,N-dimethylacrylamide, N-isopropyl acrylamide, diacetone acrylamide, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, and N-vinyl pyrrolidone among a general formula (L).

[0072]

[Formula 2]

一般式(B-1)



[0073] R21 expresses the alkyl group of a hydrogen atom or the carbon atomic numbers 1-4 among a formula. J21 expresses a divalent connection radical and expresses the benzyl which is not permuted [a methylene group, a permutation, or] or -COY-. A carbon atom is the divalent connection radical of 1-20, for example, Y expresses an alkylene group, an arylene radical, and a -O-Y'- radical and -NH-Y'-radical (Y' is an alkylene group, an arylene radical, an aralkylene group, etc.). R22 and R23 may express the alkyl group of the carbon atomic numbers 1-18, or the aralkyl radical of the carbon atomic numbers 7-18 respectively, and these alkyl groups or an aralkyl radical may have a substituent.

[0074] (C) expresses the repeat unit guided from the monomer which has ethylene nature partial saturation radicals other than (A) and (B), and which can be copolymerized among a general formula (L). As such a monomer, styrene and its derivative, acrylic ester, methacrylic ester, an acrylic acid, a methacrylic acid, a koro ton acid, a maleic acid, an itaconic acid, a fumaric acid, vinyl pyrrolidone, and vinyl ether are mentioned, and two or more of sorts of this may be used, for example.

[0075] Y expresses and, as for Z, X expresses 0 - 70-mol % 0 - 60-mol% 10 - 70-mol% among a general formula (L). However, when using two or more sorts of (C), Z expresses mol % of the sum total.

[0076] It is desirable especially desirable that it is 0.3:1-3:1 in a weight ratio, and the water-soluble cationic polymer used for this invention and a hydrophilic binder are 0.5:1-2:1. If larger [if the ratio of a water-soluble cation polymer is smaller than this ratio, the water resisting property of coloring matter and **-proof are inadequate, and] than this ratio, the absorptivity of ink will worsen and print image quality will deteriorate.

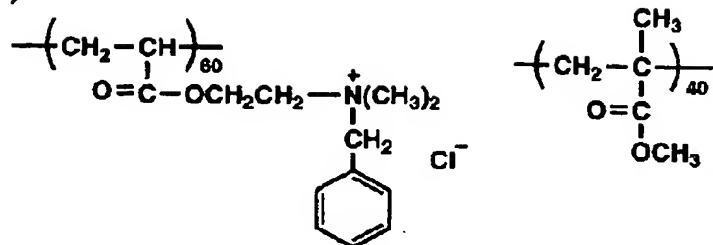
[0077] The water-soluble cationic polymer used for this invention may need to contain in the layer of the side which is most separated from a base material at least among the two-layer ink absorbing layers prepared on the base material, and it may contain it in layers other than this further. When it does not contain in the layer of the side which is most separated from a base material but contains only in the layer of the side near a base material, the water resisting property of coloring matter is inadequate, and it is not desirable.

[0078] Although the example of the cationic polymer used for this invention is shown below, it is not limited to this.

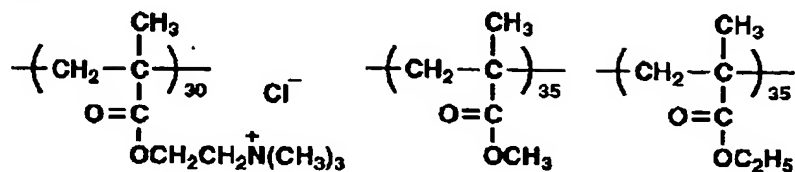
[0079]

[Formula 3]

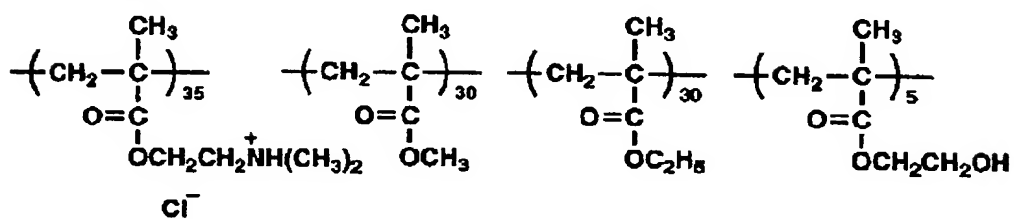
(C-1)



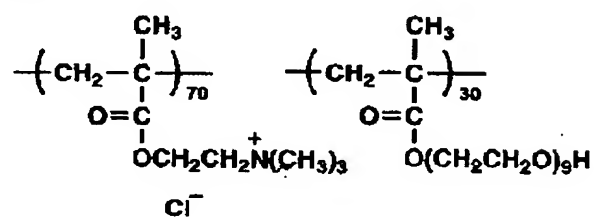
(C-2)



(C-3)



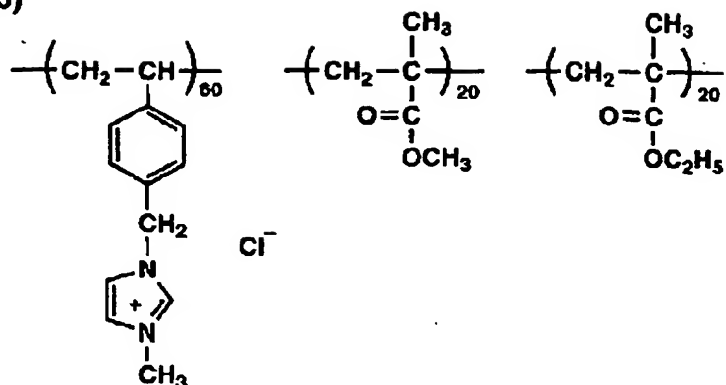
(C-4)



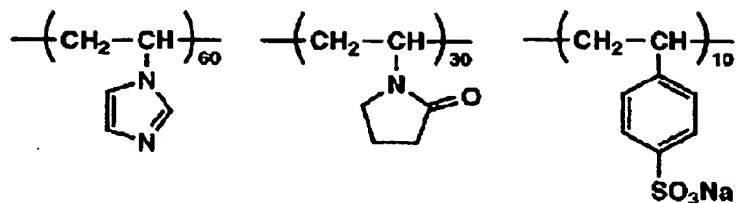
[0080]

[Formula 4]

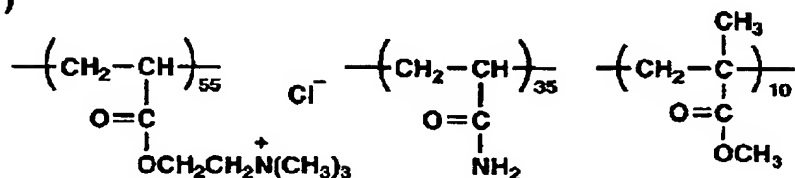
(C-5)



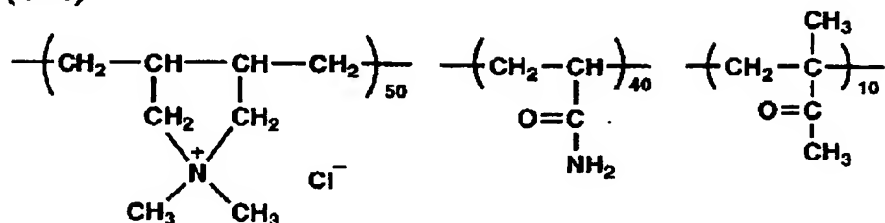
(C-6)



(C-7)



(C-8)



[0081] As for the ink jet record form of this invention, it is desirable to make at least one sort chosen from the compound which absorbs an image stabilizer and ultraviolet rays as a fading inhibitor in order to raise the lightfastness of water soluble dye contain. A water-soluble thing may be chosen and you may mix to coating liquid, and an image stabilizer may carry out oil distribution of the oil solubility thing, may make it an oil droplet, and may be mixed to coating liquid.

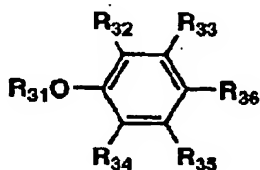
[0082] The fading inhibitor the image stabilizer used for this invention is indicated to be by JP,57-74192,A, 57-87989, 60-72785, 61-146591, JP,1-95091,A, 3-13376, etc. is mentioned.

[0083] As a desirable image stabilizer, a general formula (ST-I) and (ST-II) the compound expressed are mentioned.

[0084]

[Formula 5]

—般式(ST-I)



[0085] R31 expresses a hydrogen atom, an alkyl group, an alkenyl radical, or an aryl group among a formula, and R32, R33, R34, R35, and R36 express a hydrogen atom, a halogen atom, a cyano group, a nitro group, hydroxyl, a sulfonic group, or a univalent organic radical respectively.

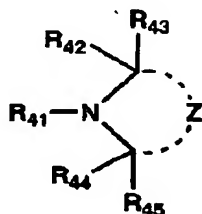
[0086] However, when R31 is a hydrogen atom, R32 and R34 are not hydrogen atoms at coincidence. Moreover, when R31 is an alkyl group, an alkenyl radical, or an aryl group, as for at least one of R32, R33, R34, R35, and the R36, -OR37 (R37 is an alkyl group or an alkenyl radical) or -N (R38)R39, (R38, and R39 are hydrogen atom, alkyl group, or alkenyl radical) respectively.

[0087] Respectively, it may join together mutually and R31, R32 and R32, R33 and R33, R36 and R36, R35 and R35, and R34, R34 and R31 may form a ring.

[0088]

[Formula 6]

一般式(ST-II)



[0089] R41 expresses a hydrogen atom, an alkyl group, an alkenyl radical, a phenyl group, hydroxyl, a sulfonyl group, a sulfinyl group, or an acyl group among a formula, and R42, R43, R44, and R45 express a hydrogen atom or an alkyl group respectively. Z expresses a nonmetal atom group required to form the nitrogen-containing heterocycle of 5 - 7 member.

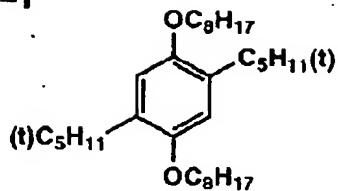
[0090] Respectively, it may join together mutually and R41, R42 and R42, R43 and R44, and R45, R44 and R41 may form a ring.

[0091] The example of the especially desirable image stabilizer used for this invention is shown below.

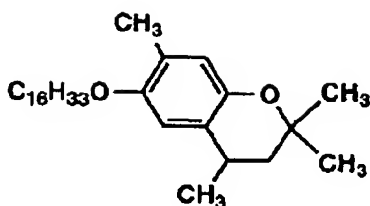
[0092]

[Formula 7]

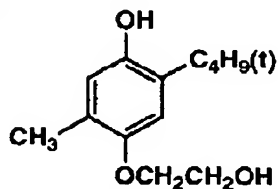
ST-1



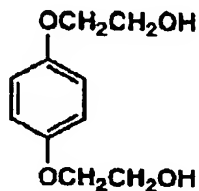
ST-2



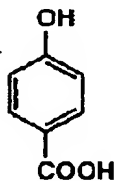
ST-3



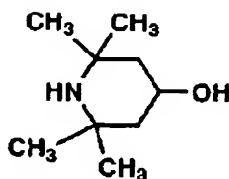
ST-4



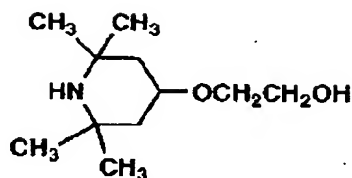
ST-5



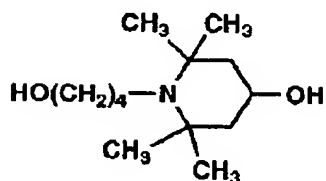
ST-6



ST-7



ST-8



[0093] The ink jet record form of this invention can make the compound which absorbs ultraviolet rays in order to raise the lightfastness of water soluble dye contain. As a compound which absorbs ultraviolet rays, the ultraviolet ray absorbent of a publication is mentioned, for example to JP,57-74193,A, 57-87988, 62-261476, etc. In order to make it ultraviolet rays not reach the water soluble dye which exists in a mordant layer, it is effective to see these ultraviolet ray absorbents from a base material rather than a mordant layer, and to make a far layer contain.

[0094] The amount of the above and the fading inhibitor used has desirable 0.01 - 5 g/m², and its 0.1 - 2 g/m² is still more desirable.

[0095] Various kinds of additives can be made to contain if needed in the ink receptiveness layer of the arbitration of the ink jet record form of this invention. For example, various well-known additives, such as pH regulators, such as the fluorescent brightener indicated by the well-known surfactant, JP,59-42993,A, a 59-52689 official report, a 62-280069 official report, a 61-242871 official report, JP,4-219266,A, etc. of various kinds, such as an anion, a cation, or Nonion, a sulfuric acid, a phosphoric acid, a citric acid, a sodium hydroxide, a potassium hydroxide, and potassium carbonate, a defoaming agent, antiseptics, a thickener, a hardening agent, an antistatic agent, and a mat agent, can also be made to contain.

[0096] In order to obtain without degrading the brittleness of the coat of high voidage, it is desirable that the dura mater of said hydrophilic binder is carried out by the hardening agent. Generally, a hardening agent is the compound which promotes the reaction of different radicals which said hydrophilic binder, the compound which has the radical which can react, or a hydrophilic binder has, according to the class of hydrophilic binder, is

chosen suitably and used. as the example of a hardening agent — for example, an epoxy system hardening agent (diglycidyl ethyl ether —) Ethylene glycol diglycidyl ether, 1,4-butanediol diglycidyl ether, A 1, 6-diglycidyl cyclohexane, N, and N-diglycidyl-4-glycidyloxy aniline, aldehyde system hardening agents (formaldehyde —), such as sorbitol polyglycidyl ether activity halogen system hardening agent [, such as glyoxal,], (2, and 4-dichloro-4-hydroxy - 1, 3, and 5-s-triazine etc. —) — An activity vinyl system compound, way acids (1, 3, 5-tris acryloyl-hexahydro-s-triazine, bisvinyl-sulfonyl methylether, etc.) and the salt of those, way sand, aluminum alum, etc. are mentioned.

[0097] As an especially desirable hydrophilic binder, when using polyvinyl alcohol and its derivative, it is the hardening agent chosen from a boric acid and its salt. By this invention, as a boric acid or its salt, the oxygen acid which uses a boron atom as a neutral atom, and its salt are shown, and orthoboric acid, 2 boric acids, metaboric acid, the tetraboric acid, 5 boric acids, 8 boric acids, and those salts are specifically contained.

[0098] Although the amount of the above-mentioned hardening agent used changes by the ratio to the class of hydrophilic binder, the class of hardening agent, the class of non-subtlety particle, and a hydrophilic binder etc., it is 5-100mg preferably 1-200mg per hydrophilic binder 1g in general.

[0099] The above-mentioned hardening agent may be added in the coating liquid which forms the layer of others which reach among the coating liquid of the opening stratification, or adjoin an opening layer in case the coating liquid which constitutes an opening layer is applied. Or although carrying out the overcoat of the hardening agent solution etc. can carry out hardening agent the coating liquid of not containing [which applies the coating liquid which forms said opening layer on the base material which has applied the coating liquid which contains a hardening agent beforehand, or forms an opening layer further], after spreading desiccation and a hardening agent can be supplied to an opening layer It is desirable to supply a hardening agent to to add a hardening agent and to form an opening layer into the coating liquid of the layer which adjoins the coating liquid or this which forms an opening layer from the effectiveness on manufacture preferably, and coincidence.

[0100] Although it is desirable to contain various drops in order to improve the brittleness of the coat of the ink absorption layer of the ink jet record form of this invention, the solubility over the water in a room temperature can make about 0.01 or less % of the weight of hydrophobic high-boiling point organic solvents (a liquid paraffin, dioctyl phthalate, tricresyl phosphate, silicone oil, etc.) and a polymer particle (particle to which the one or more sort polymerization of the monomers, such as styrene, butyl acrylate, a divinylbenzene, butyl methacrylate, and hydroxyethyl methacrylate, was carried out) contain as such an oil droplet. Such an oil droplet can be preferably used ten to 50% of the weight to a hydrophilic binder. It is also desirable that molecular weight contains 300 or less polyols to the brittleness of a coat. As such polyols, ethylene glycol, a diethylene glycol, triethylene glycol, tetraethylene glycol, a polo pyrene glycol, a glycerol, 1,6-hexanediol, 1, 2-cyclohexane diol, a with a molecular weight of 300 or less polyethylene glycol, or a polyethylene glycol is mentioned.

[0101] As a base material of the ink jet record form of this invention, a thing well-known as a record form for ink jets can be used suitably conventionally.

[0102] The thing of a property which bears the radiant heat when being able to mention the film which consists of ingredients, such as polyester system resin, diacetate system resin, triacetate system resin, acrylic resin, polycarbonate system resin, polyvinyl chloride system resin, polyimide system resin, cellophane, and celluloid, a plate, a glass plate, etc. as a transparence base material, for example, and being used as an OHP also in this is desirable, and especially polyethylene terephthalate is desirable. As thickness of such a transparent base material, about 10-200 micrometers is desirable.

[0103] Moreover, although what carried out opacification processing of the sheet which consists of common paper, a synthetic paper, resin covering paper, cloth, wood, a metal, etc. as a base material to be used, for example, a plate, and the above-mentioned translucency base material with the well-known means can be mentioned when there is no transparent need The so-called White pet which comes to add white pigments to the resin covering paper (the so-called RC paper) which has the polyolefin resin enveloping layer which added white pigments etc. at least to one side of a base paper, and polyethylene terephthalate is desirable. It is desirable to perform corona discharge treatment, undercoating processing, etc. to a base material in advance of spreading of an ink absorbing layer for the purpose, such as to enlarge bond strength of a base material and an ink television layer. Furthermore, the record form of this invention does not necessarily need to be colorlessness, and may be a colored record form.

[0104] Although it can carry out by choosing suitably the approach of applying the layer containing the non-subtlety particle of this invention on a base material from a well-known approach, the extrusion coat method which uses a hopper the roll coat method, the rod bar coat method, the air knife coat method, a spray coating method, the curtain coat method, or given in U.S. Pat. No. 2681294 is used preferably.

[0105] Moreover, after it cools and the gel state takes after applying on a base material as indicated by JP,6-64306,A in using the hydrophilic binder in which sol gel transformation, such as gelatin, and a gelatin derivative, a kappa carrageenan, is possible, you may carry out by the approach of drying by the cold dry cleaning method.

[0106] In case image recording is carried out using the ink jet record form of this invention, the record approach

which used water color ink is used.

[0107] The water color ink said by this invention is the following coloring agent and a solvent object, and a record liquid that consists of other additives. Water soluble dye, such as direct dye well-known as a coloring agent at an ink jet, acid dye, basic dye, reactive dye, or a food dye, can be used.

[0108] As a solvent of water color ink, water and water-soluble, various organic solvents For example, methyl alcohol, isopropyl alcohol, n-butyl alcohol, Alcohols, such as tert-butyl alcohol and isobutyl alcohol; Dimethylformamide, Amides, such as dimethylacetamide; Ketones, such as an acetone and diacetone alcohol, or a ketone-alcohol; tetrahydrofuran, Ether, such as dioxane; Polyalkylene glycols; ethylene glycol, such as a polyethylene glycol and a polypropylene glycol, Propylene glycol, a butylene glycol, triethylene glycol, 1, 2, 6-hexane triol, thiodiglycol, hexylene glycol, Polyhydric alcohol, such as a diethylene glycol, a glycerol, and triethanolamine; Ethylene glycol methyl ether, The low-grade alkyl ether of polyhydric alcohol, such as the diethylene-glycol methyl (or ethyl) ether and the triethylene glycol monobutyl ether, is mentioned.

[0109] Also in the water-soluble organic solvent of these many, the low-grade alkyl ether of the polyhydric alcohol of polyhydric alcohol, such as a diethylene glycol, triethanolamine, and a glycerol, and the triethylene glycol monobutyl ether etc. is desirable.

[0110] As an additive of other water color ink, a pH regulator, a sequestering agent, an antifungal agent, a viscosity controlling agent, a surface tension regulator, a wetting agent, a surfactant, a rust-proofer, etc. are mentioned, for example.

[0111] In order to make wettability to a record form good, as for water-color-ink liquid, in 20 degrees C, it is desirable to have the surface tension of 30 – 50 dyn/cm within the limits preferably 25 to 60 dyn/cm.

[0112] the ink jet recording method in which the regurgitation [water color ink] of the ink regurgitation method at the time of carrying out image recording using the ink jet record form of this invention is possible — it is — ****ing — for example, "ink jet record technical trend" Nakamura [Koichi] editing — recording methods, such as a continuation injection electric charge control system, a method on demand, etc. of a publication, can be used for work (Japanese Science-information, 1995) p.1–14. However, bigger effectiveness can be acquired by using it also in these, applying to the recording method of a method on demand.

[0113]

[Example] Although the example of this invention is given and explained below, this invention is not limited to these examples. In addition, in an example, "%", as long as there is no notice especially, oven-dry-weight % is shown, and an addition shows the amount per two 1m of ink jet record forms respectively.

[0114] The paper base material which covered stencil paper both sides of example 1100 g/m² with polyethylene (it is 7% of the weight of anatase mold titanium-dioxide content in the polyethylene layer by the side of 140 micrometers in thickness, and a recording surface.) In [having the layer which contains alkali treatment gelatin 1.2 g/m² and a hardening agent as a back layer in the rear-face side of a recording surface], coincidence multistory spreading desiccation was respectively performed for coating liquid -2 to the recording surface side by 100 micrometers of humid thickness as coating liquid -1 and the upper layer, and the record form 1 was obtained. The void volume of this coat was about 25 ml/m².

[0115]

[Coating liquid -1]

Pure water 1000ml Particle silica with a mean particle diameter of about 7nm 150g Polyvinyl alcohol of average degree of polymerization 3500 (5% water solution)

(Whenever [saponification] 89%) 500g (it indicates to Table 1) Cationic polymer (it indicates to Table 1) surfactant -3 1.2g Borax (4% water solution) the 20ml above-mentioned liquid — a high-speed homogenizer — distributing — white — translucent coating liquid was obtained.

[0116]

[Coating liquid -2]

Pure water 1000ml Particle silica with a mean particle diameter of about 7nm 150g Polyvinyl alcohol of average degree of polymerization 3500 (5% water solution)

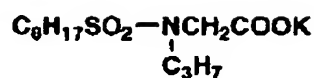
(Whenever [saponification] 89%) 500g (it indicates to Table 1) Cationic polymer (it indicates to Table 1)

Surfactant -1 0.70g Surfactant -2 0.30g Borax (4% water solution) The structure of the compound used by 20ml above is shown below.

[0117]

[Formula 8]

界面活性剤-1



界面活性剤-2



界面活性剤-3



[0118] The high-speed homogenizer distributed the above-mentioned liquid, and translucent white coating liquid was obtained.

[0119] As shown in Table 1, the weight ratio of addition, a cation polymer, and all polyvinyl alcohol was changed for the primary particle diameter of the silica to be used, the water-soluble cation polymer, and the fading inhibitor, and also the record forms 2-19 as well as the record form 1 were created. Both the desiccation thickness and void volume of a record form that were done were also shown in Table 1.

[0120]

[Table 1]

記録用紙	第 1 層		第 2 層		全 層	
	シリカ 1 次粒子径 (nm)	カチオン 性ポリマ ー	カチオン 性ポリマ ー	退色防 止剤	カチオン性ポ リマー/PV A (重量比)	空隙容量 ml/m ²
1 (本発明)	7	—	C-2	—	0.7	25.0
2 (本発明)	7	—	C-6	—	0.7	24.1
3 (本発明)	7	—	C-7	—	0.7	24.5
4 (本発明)	7	C-2 *	C-2 *	—	0.7	24.8
5 (本発明)	7	—	C-2	—	0.2	25.7
6 (本発明)	7	—	C-2	—	0.5	25.3
7 (本発明)	7	—	C-2	—	2	23.8
8 (本発明)	7	—	C-2	—	3	23.0
9 (本発明)	7	—	C-2	—	4	21.5
10 (本発明)	7	—	C-6	①	0.7	23.8
11 (本発明)	7	—	C-6	②	0.7	23.7
12 (本発明)	7	—	C-6	③	0.7	23.3
13 (本発明)	12	—	C-7	—	0.7	24.1
14 (本発明)	20	—	C-7	—	0.7	23.1
15 (比較例)	40	—	C-7	—	0.7	20.5
16 (本発明)	7	—	I	—	0.7	25.2
17 (比較例)	7	C-2	—	—	0.7	24.7
18 (比較例)	7	—	II	—	0.7	19.8
19 (比較例)	7	—	—	—	0.7	19.8

[0121] *: the record form 4 divided the cationic polymer into the 1st layer and the 2nd layer ana, and added.

[0122] **: the record form 10 added 40ml (distributed object -1) of following.

[0123] **: the record form 11 added instantiation compound ST-4 [10g].

[0124] **: the record form 12 added instantiation compound ST-5 [10g].

[0125] (Distributed object -1) The solution 1 and solution 2 of the following presentation were prepared, and it mixed, and distributed in the ultrasonic disperser.

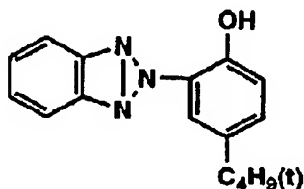
[0126]

Solution 1 Ultraviolet ray absorbent -1 1g G i-DESHIRU phthalate 1g Ethyl acetate 5ml solution 2 Gelatin 0.5g Surfactant -4 (tree i-propyl naphthalene sulfo N acid sodium) 0.2g pure water Structure of the compound used by 15ml above It is shown below.

[0127]

[Formula 9]

紫外線吸収剤-1



[0128] About each obtained ink jet record form, using ink jet printer MJ[by Seiko Epson, Inc.]-900C, the evaluation pattern was printed and the following items were evaluated.

[0129] (1) Homogeneity was made to breathe out and it recorded so that it might become 30% of the amount of the maximum ink, respectively, and 20 red-reflex concentration of the solid section was measured using the microdensitometer (aperture =200micrometerphi), and the value of ink absorptivity yellow and cyanogen broken by average reflection density in quest of the standard deviation of the variation in the concentration was calculated.

[0130] When ink absorptivity is good, the value of non-Lycium chinense becomes [nonuniformity] small at an image, but if ink absorptivity falls, this each other liquid ink drops will cause beading mutually in the record paper, it will become nonuniformity, and this value will increase.

[0131] (2) Visual evaluation of neglect and the imprint degree of the ink to a rear face was carried out on the following criteria for 1 minute, having applied the rear face of after [of an after / printing] 5 minutes, and a record form, and the load of superposition and 120 g/cm² for 60% printing section of drying yellow and a Magenta.

[0132]

O : — completely — imprint-less O: — although imprinted slightly — a printing image — almost — effect-less
x: — after a lot of ink carried out the dipping of the effect size (3) water-resisting-property printing sample to the imprint and the printing image for 10 minutes underwater [20-degree C], it dried and residual concentration compared the water resisting property of the printing image of the maximum-density part of a Magenta. It evaluated in four steps of OO**x from what has high concentration.

[0133] (4) The sample after damp-proof printing was saved for three days after two-week preservation and by 60-degree-C80%RH by 23 degrees C and 20%RH, and the blot degree of each color was evaluated. evaluation —

O: — completely — blot-less O:blot width of face — less than (a blot is accepted slightly visually) about 0.1mm

** : Blot width of face is 0.1mm - less than (permission is visually impossible) 0.5mm.

x: More than 0.5mm (with no value as an image)

(5) The sample of the maximum-density part of a light-fast Magenta was asked for the reflection density ratio before 20-hour Mitsuteru putting, and an exposure after an exposure in xenon fade meter.

[0134] (6) Gloss was measured for the glossiness printing side 60 degrees using the deflection glossmeter (VGS-1001DP) by Nippon Denshoku Industries Co., Ltd.

[0135] The obtained result is shown in Table 2.

[0136]

[Table 2]

記録用紙	インク吸収性	乾燥性	耐水性	耐湿性	耐光性	光沢度 (%)
1 (本発明)	0.10	○	○	○	75	57
2 (本発明)	0.10	○	○	○	70	50
3 (本発明)	0.10	○	○	○	70	51
4 (本発明)	0.10	○	◎	◎	70	55
5 (本発明)	0.08	◎	△	△	80	65
6 (本発明)	0.09	○	○	○	75	60
7 (本発明)	0.12	○	◎	○	70	50
8 (本発明)	0.13	○	◎	○	65	47
9 (本発明)	0.14	△	◎	◎	65	40
10 (本発明)	0.10	○	○	○	90	50
11 (本発明)	0.10	○	○	○	92	51
12 (本発明)	0.10	○	○	○	95	50
13 (本発明)	0.10	○	○	○	75	51
14 (本発明)	0.11	○	○	○	70	47
15 (比較例)	0.18	△	○	○	70	29
16 (本発明)	0.10	○	△	○	70	49
17 (比較例)	0.10	○	△	×	80	60
18 (比較例)	0.17	△	○	△	60	52
19 (比較例)	0.09	◎	×	×	70	65

[0137] Table 2 shows that the ink jet record form of this invention has good ink absorptivity, drying, a water resisting property, moisture resistance, lightfastness, and glossiness.

[0138] Glossiness falls greatly and, as for the record form 17 which added the cationic polymer only in the lower layer, the record form 18 which added the cation polymer which is not water solubility, and the record form 19 which has not added the cationic polymer, a water resisting property and moisture resistance fall [the record form 15 using a silica with a large primary particle size] greatly.

[0139] Although it was opaque and the case where a glossy paper base material was used was explained by this example, the suitable ink jet record form for the application using transparency of CFM used for color displays, such as what observes a record image by projection to a screen etc., and the color-separation version at the time of creating the positive version of color printing or liquid crystal, by optical instruments, such as a slide and OHP, can be offered by using a base material with translucency.

[0140] Moreover, although the case where it mainly uses for an ink jet method has been explained about the record sheet of this invention, it can use suitable for record by record devices, such as various writing materials, a pen plotter, etc. which use water color ink besides an ink jet method.

[0141]

[Effect of the Invention] As mentioned above, if the configuration of the ink jet record form of this invention is used, in printing by water color ink, maintaining high glossiness, moreover good ink absorptivity can be attained and a water resisting property, moisture resistance, and lightfastness can carry out formation record of the good high-definition image.

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PRIOR ART

[Description of the Prior Art] although ink jet record makes the minute drop of ink fly by various working principles, and is made to adhere to record sheets, such as paper, and an image, an alphabetic character, etc. are recorded, a high speed, the low noise, and multiple-color-izing are comparatively easy — etc. — it has the advantage. About the blinding of a nozzle and the maintenance which had become a problem from the former by this method, from both sides of ink and equipment, amelioration progresses and it has spread through various fields, such as various printers, facsimile, and a computer terminal, quickly in current.

[0003] As a record form used by this ink jet recording method, also when a printing dot laps [that a color tone is brightly skillful and absorption of ink] early, the diffusion to the longitudinal direction of ink flowing out or not spreading and a printing dot is not large [the concentration of a printing dot is high, and] beyond the need, and it is required that the circumference should be smooth and should not fade etc.

[0004] Since it becomes nonuniformity, and the color of each other in the border area of a color which a drop causes a HAJIKI phenomenon on a record form, and is different spreads and it is easy to reduce image quality greatly in case the liquid ink drop of two or more colors laps and is recorded, when especially ink rate of absorption is slow, it is required to give ink absorptivity high as a record form.

[0005] In order to solve these problems, very many techniques are proposed from the former.

[0006] As the pigment in the record form which carried out humidity of the coating for surface treatment to the low size stencil paper indicated by JP,52-53012,A, the record form which prepared the coated layer of ink absorptivity in the support surface indicated by JP,55-5830,A, and ****-ed indicated by JP,56-157,A The record form containing non-colloid silica powder, the record form which used together the inorganic pigment indicated by JP,57-107878,A and the organic pigment, The record form which has two hole distribution peaks indicated by JP,58-110287,A, The record form which consists of a vertical two-layer porous layer indicated by JP,62-111782,A, The record form which has the indeterminate form crack indicated by JP,59-68292,A, 59-123696, the 60-18383 official report, etc., The record form which has the impalpable powder layer indicated by JP,61-135786,A, 61-148092, the 62-149475 official report, etc., JP,63-252779,A, JP,1-108083,A, 2-136279, The record form containing the pigment which has the specific physical-properties value indicated by 3-65376, 3-27976, etc., or a particle silica, JP,57-14091,A, 60-219083, 60-210984, 61-20797, 61-188183, JP,5-278324,A, 6-92011, 6-183134, 7-137431, The record form containing particle silicas, such as a colloid silica indicated by 7-276789 etc., And JP,2-276671,A, 3-67684, 3-215082, A large number are known for the record form containing the hydrated alumina particle indicated by 3-251488, 4-67986, 4-263983, the 5-16517 official report, etc.

[0007] However, since many ink absorbing layers with many openings will have irregularity with micro interface with air and coat front face, the incident light to an ink absorbing layer is scattered about or transparency is barred when an ink absorbing layer absorbs ink or it consists of only layers which have many openings for holding, it becomes or tends to be hard to come out opaquely lusterless.

[0008] Moreover, in order to form an opening, there is a fault out of which the smooth nature on the front face of a coat by own irregularity of a pigment or the irregularity of the secondary floc of a pigment falls, and gloss cannot come easily.

[0009] On the other hand, many ink jet record forms of the type which absorbs ink and is held in a swelling operation of the binder of an ink absorption layer are also known, without preparing an opening into a coat.

[0010] For example, many the recording papers, films, etc. which applied hydrophilic binders, such as gelatin, casein, starch, an alginic acid, polyvinyl alcohol, various kinds of denaturation polyvinyl alcohol, a polyvinyl pyrrolidone, polyethylene oxide, polypropylene oxide, a carboxymethyl cellulose, HIDOROKI ethyl cellulose, a dextran, and a pullulan, on the base material as binders are known from the former.

[0011] Although these record forms are inferior in ink absorptivity compared with the record form which has the above-mentioned opening, high glossiness and optical density, and a clear image are obtained, and they are useful as a high-definition record application.

[0012] since it differed in the color printing paper in which a coloring matter molecule be distribute in the state of a high-concentration particle in oils and a coloring matter molecule existed between the inside of a binder , and an opening independently , a fault which waterdrop be pour on a recording surface , or spread when it be

save under high humidity conditions the printing back for a long period of time, or be easy flow out be in various kinds of ink jet record forms suitable for the water-soluble above-mentioned ink.

[0013] In order to improve the water resisting property and moisture resistance of this coloring matter, the various methods of making coloring matter fix in a binder from the former are proposed. Especially an effective means is the approach of adding as a particle latex by using as a uniform water solution the polymer which has the nitrogen atom of the 3rd class or the 4th class.

[0014] For example, the ink jet record form applied on stencil paper or a polyethylene terephthalate film base material by using as an ink absorbing layer the coating liquid which uses gelatin as some binders at JP,57-36692,A, and contains a basic mordant is indicated.

[0015] The water-color-ink record form which infiltrated polyethyleneimine into paper is indicated by JP,53-49113,A.

[0016] The record material which has the electrolyte polymer which has a cation or an anion radical is indicated by JP,58-24492,A.

[0017] The 1st class thru/or tertiary amine, or quarternary ammonium salt is contained in an ink absorbing layer, and the charge of a recorded material which has pH of an ink maintenance layer in 2-8 is indicated by JP,63-224988,A.

[0018] The ink jet record form which has a layer containing the polymer which has the hydrophilic polymer mordant which has the 3rd class or the 4th class nitrogen atom, and a hydrophilic radical is indicated by JP,63-307979,A.

[0019] The record ingredient which made the organic base of polyethyleneimine contain in the coating layer in a base material or on a base material is indicated by JP,59-198186,A and 59-198188.

[0020] The ink jet record approach using the ink containing a specific color and the record ingredient containing polyamine etc. is indicated by JP,60-46288,A.

[0021] The ink jet record form containing the poly allylamine is indicated by JP,61-61887,A, 61-72581, 61-252189, and 62-174184.

[0022] The ink jet record ingredient containing the polymer which has an intermolecular hydrogen bridge, and the polymers (a polyethylene glycol, polyvinyl pyrrolidone, etc.) which do not have a hydrogen bond nature machine among molecules (gelatin, polyethylene RENIMIN, etc.) is indicated by JP,61-172786,A.

[0023] The ink jet record form which applies or infiltrated the cationic polymer and the cationic surface active agent on the base material is indicated by JP,63-162275,A.

[0024] The record form which superimposed the color fixing layer which uses a quarternary-ammonium-salt polymerization object and cation denaturation polyvinyl alcohol as a principal component on a plastics base material, and the color transparency and ink absorption layer which were prepared on it on JP,6-143798,A is indicated.

[0025] Furthermore, JP,59-20696,A, 59-33176, 59-33177, 59-96987, 59-155088, 60-11389, 60-49990, 60-83882, 60-109894, 61-277484, 61-293886, 62-19483, 62-198493, 63-49478, 63-115780, 63-203896, 63-274583, 63-280681, The nitrogen atom of the 3rd class or the 4th class of specification [63-260477, JP,1-9776,A, 1-20188, 1-24784, 1-40371, 3-133686, 6-234268, and 7-125411] respectively Adding the polymer or compound to contain all over an ink absorbing layer is indicated.

[0026] However, although the water resisting property of coloring matter improves according to the above-mentioned conventional approach, that to which lightfastness falls is most.

[0027] Moreover, a polymer of a certain kind had the fault that cost was high, and had the fault of spreading with it not being performed, or being unable to carry out little deer use. [low compatibility with the binder to be used and] [good]

[0028] Although the record sheet which makes the deck-watertight-luminaire-ized agent of a coat exist in the ink absorption layer which becomes JP,7-125412,A from a binder and a filler, and carries out localization of the fixing agent of an ink color into the front face of this ink absorption layer and/or a surface, and its manufacture approach were indicated, it is characterized by to carry out the overcoat of the color fixing agent which cannot be added in an ink absorption layer to an absorption layer, and there was a fault with the high cost by letting a spreading process pass twice.

[0029] Although the record form with which a laminating and JP,7-242056,A prepare an ink absorption layer in JP,5-124329,A at the color fixing layer which uses a quarternary-ammonium-salt polymerization object as a principal component for the anionic layer of a pigment and a water-soluble binder layer at JP,5-131742,A, and prepare the water meltable alcoholic insoluble polymer content layer of a silica particle and the amount of specification one by one on a cationic polymer layer at a quarternary-ammonium-salt water solubility polymer content absorption layer was indicated, ink absorptivity and a coloring matter water resisting property were able to say that neither was enough.

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EFFECT OF THE INVENTION

[Effect of the Invention] As mentioned above, if the configuration of the ink jet record form of this invention is used, in printing by water color ink, maintaining high glossiness, moreover good ink absorptivity can be attained and a water resisting property, moisture resistance, and lightfastness can carry out formation record of the good high-definition image.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention is offering the ink jet record form which can carry out formation record of the high-definition image which is made in view of the above-mentioned actual condition, and the purpose of this invention moreover has high ink absorptivity, maintaining high glossiness in printing by water color ink, and was excellent in a water resisting property, moisture resistance, and lightfastness.

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MEANS

[Means for Solving the Problem] The above-mentioned purpose of this invention is attained by the following configuration.

[0032] (1) the ink jet record form which has at least the two-layer ink absorbing layer prepared a base material and on it — setting — this ink absorbing layer — an average of 1 — the ink jet record form characterized by containing a water-soluble cationic polymer in the layer which contained the silica system particle and the hydrophilic binder not more than order particle diameter 20nm, and is most separated from the base material by the side of an ink absorbing layer at least.

[0033] (2) The ink jet record form given in (1) characterized by being at least one as which said hydrophilic binder is chosen from polyvinyl alcohol and its derivative.

[0034] (3) (1) characterized by said water-soluble cationic polymer and hydrophilic binder being 0.3:1–3:1 in a weight ratio, or an ink jet record form given in (2).

[0035] (4) The ink jet record form of (1) – (3) characterized by all ink absorbing layers containing said water-soluble cationic polymer given in any 1 term.

[0036] (5) The ink jet record form of (1) – (4) characterized by containing at least one sort chosen from the compound which absorbs an image stabilizer and ultraviolet rays as a fading inhibitor given in any 1 term.

[0037] Hereafter, this invention is explained to a detail.

[0038] High ink absorptivity is acquired by the opening in which the ink jet record form of this invention is formed of the binder and silica system particle of a hydrophilic property.

[0039] Generally as the formation approach of a typical opening with a solid-state particle and a hydrophilic binder, the following approaches can be considered.

[0040] (1) Apply the coating liquid containing a porosity solid-state particle and a hydrophilic binder on a base material. As opposed to the approach (2) hydrophilic-property binder which forms an opening between the inside of a porosity particle, or a particle The coating liquid containing the solid-state particle which has the volume more than equivalence (preferably 10 or more times) in general, and a hydrophilic binder is applied on a base material. Between solid-state particles The approach the approach (3) mean particle diameter which creates an opening makes solid-state particle about 0.1 micrometers or less condense at the time of coating liquid preparation or coat formation, forms a secondary particle or the three-dimensional structure, and creates an opening.

[0041] Although the approach (1) was generally excellent in ink absorptivity and it was widely used by coat paper etc. from before, the porosity solid-state particle was a particle with the big particle diameter of the micron order which the secondary most is condensing so that it might be represented by the synthetic indeterminate form silica, and was difficult to acquire glossiness sufficient in just the opening layer obtained by this approach.

[0042] Although excelled in ink absorptivity, since a solid-state particle was a high ratio to a hydrophilic binder, when the embrittlement of a coat was not avoided but unabsorbent base materials, such as plastic film, were used especially, various problems, such as a crack of an absorption layer and powder omission, might arise said approach (2) at the time of a manufacture process or use.

[0043] In this invention, a desirable mode is said approach (3). This approach is the approach of forming a flocculation condition by the solid-state particle, and forming the network structure into a coat, and into the water solution which contains a hydrophilic polymer preferably, the primary ultrafine particle in a distributed condition is formed via the condition of condensing each other, where a point of contact is restricted comparatively. that such a flocculation condition is linear or the condition that what formed floc in the shape of branching was distributed in the water solution — or the condition of such flocs condensing each other further and taking the three-dimension network structure in a water solution is included. Even if it is which case, detailed structure can be formed into the formed coat by carrying out spreading desiccation of this water solution on a base material.

[0044] Thus, in general, from the magnitude of a primary particle, the magnitude of the detailed opening in the obtained coat is about several times those magnitude of this, and has the description which is the opening of detailed magnitude.

[0045] It is formed in the water solution which has the approach of being hard to condense a primary particle to each other, carrying out ultralow volume addition of the hydrophilic polymer which accelerates condensation of a particle in the water solution containing the hydrophilic polymer which can exist in stability as an approach of forming such a flocculation condition, for example, and forming condensation slightly, or the water-soluble polymer which can perform a primary particle front face and weak coupling.

[0046] Especially in this invention, it is desirable from that the latter approach tends to form the amount of an opening in stability that it is comparatively easy to control, and more amounts of openings being obtained as compared with the amount of the particle to be used, and since a coat with the still higher glossiness of a coat is obtained, the particle diameter (first [an average of] particle diameter) of a primary particle uses a silica particle 20nm or less.

[0047] As a hydrophilic binder used for the ink jet record form of this invention Gelatin or a gelatin derivative, a polyvinyl pyrrolidone (about 200,000 or more have desirable average molecular weight), A pullulan, polyvinyl alcohol, or its derivative (about 20,000 or more have desirable average molecular weight), A polyethylene glycol (100,000 or more have a desirable mean molecular weight), a carboxymethyl cellulose, Hydroxyethyl cellulose, a dextran, a dextrin, polyacrylic acid, and its salt, An acrylamide system polymer, an agar, a kappa carrageenan, lambda-carrageenan, iota-carrageenan, xanthene gum, locust bean gum, an alginic acid, A polyalkylene oxide system copolymerization nature polymer given in gum arabic, a pullulan, JP,7-195826,A, and 7-9757, a water-soluble polyvinyl butyral, Or polymers, such as independent or a copolymer which repeats and has these vinyl monomers of the vinyl monomer which has the carboxyl group and sulfonic group of a publication, can be mentioned to JP,62-245260,A. These hydrophilic binders may be used independently and may use two or more sorts together.

[0048] In the ink jet record form of this invention, the case where primary [an average of] particle diameter uses polyvinyl alcohol or denaturation polyvinyl alcohol as a hydrophilic binder to a silica particle as a particle 20nm or less is desirable. In this case, hydrogen bond with weak silanol group of a particle silica front face and hydroxyl group of vinyl alcohol is performed, and said flocculation object is formed good.

[0049] Especially as said silica particle, a 6-15nm thing is the most desirable. Moreover, as a secondary particle which these connected, it is desirable to make it preferably set to about 30-100nm 20-200nm.

[0050] The particle silica compounded by the synthetic approach by which such a particle silica is called a usual gaseous-phase method given [for example,] in JP,60-204390,A is used preferably. Moreover, this silica particle may be the object which cation denaturation could be made [which was] like a silane coupling agent in the front face, and was processed by aluminum, calcium, Mg, Ba, etc.

[0051] The hydrophilic binder preferably used by this invention is polyvinyl alcohol or its derivative. Polyvinyl alcohol or its derivative is the polyvinyl alcohol or cation denaturation polyvinyl alcohol of completeness or partial saponification. one especially desirable also in polyvinyl alcohol — whenever [saponification] — 80 or more parts — or full saponification is carried out. moreover, the viewpoint which improves coat brittleness to average degree of polymerization — 500-3500 — the thing of 1000-3500 is used especially preferably.

[0052] Moreover, it is polyvinyl alcohol which has the 1-3rd class amino group which is indicated by JP,61-10483,A, for example, and the 4th class ammonium in the principal chain of the above-mentioned polyvinyl alcohol, or a side chain as cation denaturation polyvinyl alcohol.

[0053] By this approach, as a hydrophilic binder, it is desirable in order for 1500 or more to carry out especially polymerization degree especially of the polyvinyl alcohol used preferably for not causing a crack to a coat 1000 or more.

[0054] Here, the ratios of polyvinyl alcohol and the above-mentioned silica are 1:10-1:1 in general, and the range of them is 1:7-1:2 preferably.

[0055] It explains briefly [below] about the approach of forming the coat which contains a flocculation object using polyvinyl alcohol and a particle silica.

[0056] In the polyvinyl alcohol water solution (in general 5 - 15%) which maintained pH at 6-8, and the temperature of about 40 degrees C, it adds gradually, strong-agitating silica dispersion liquid (in general 5 - 15%), and an ultrasonic disperser, a high-speed homogenizer, etc. distribute after addition termination. In this case, in order to prepare uniform coating liquid, water miscibility organic solvents, such as various kinds of surfactants, and a methanol, an acetone, may be used if needed. Subsequently, after adding various kinds of additives, it adjusts to target viscosity required for spreading, and the coat which has the above-mentioned opening by applying and drying by the well-known approach on a base material is obtained.

[0057] Although other hydrophilic binders can be made to contain in said opening layer, as for those hydrophilic binders, it is preferably desirable that it is 20 or less % of the weight in general to said polyvinyl alcohol or its derivative.

[0058] A well-known solid-state particle inorganic [various kinds of] or organic can be conventionally used for the ink absorption layer of the ink jet record form of this invention in an ink jet record form as a solid-state particle in the range which does not spoil the effectiveness of this invention. As an example of the non-subtlety

particle used, white inorganic pigments, such as precipitated calcium carbonate, whiting, a magnesium carbonate, a kaolin, clay, talc, a calcium sulfate, a barium sulfate, a titanium dioxide, a zinc oxide, zinc hydroxide, zinc sulfide, zinc carbonate, a hydrotalcite, aluminum silicate, the diatom earth, a calcium silicate, a magnesium silicate, synthetic amorphous silica, a gaseous-phase method silica, colloidal silica, an alumina, a colloidal alumina, pseudo-boehmite, an aluminum hydroxide, a lithopone, a zeolite, and a magnesium hydroxide etc. can be mentioned

[0059] On the other hand as an example of an organic particle, polystyrene, polyacrylic ester, polymethacrylic acid ester, polyacrylamides, polyethylene, polypropylene, a polyvinyl chloride, polyvinylidene chlorides or these copolymers, a urea-resin, or melamine resin is mentioned.

[0060] The water-soluble cationic polymer for improving the absorptivity of ink, the water resisting property of coloring matter, and damp-proof both in the ink jet record form of this invention is used.

[0061] For example, the absorptivity of ink may be spoiled by the approach of adding the particle latex of the polymer which has a nitrogen atom of the 3rd class or the 4th class like a JP,57-36692,A publication, and it is not desirable. Although a reason is not clear, probably it is presumed for a latex particle to bar the opening formation by the hydrophilic binder and the silica system particle. As a water-soluble cation polymer used for this invention Polyethyleneimine, JP,59-20696,A, 59-33176, 59-33177, 59-155088, 60-11389, 60-49990, 60-83882, 60-109894, 62-198493, 63-49478, 63-115780, The polymer which has the 1-3rd class amino group indicated by 63-280681, JP,1-40371,A, 6-234268, 7-125411, etc. and a quarternary-ammonium-salt radical is used preferably.

[0062] Among these especially the water-soluble polymer used preferably is expressed with the following general formula.

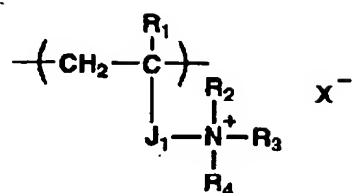
[0063] General formula (L)

(A) A is expressed with following general formula (A-1) - (A-8) among an X-(B) Y-(C) Z general formula (L).

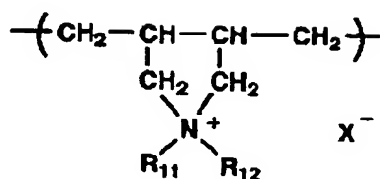
[0064]

[Formula 1]

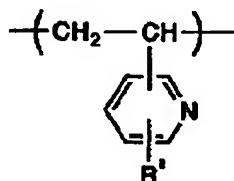
一般式(A-1)



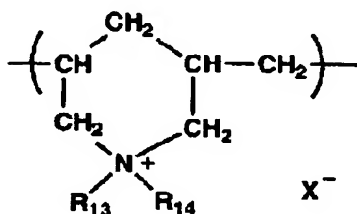
一般式(A-6)



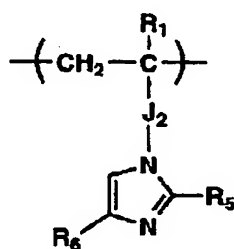
一般式(A-2)



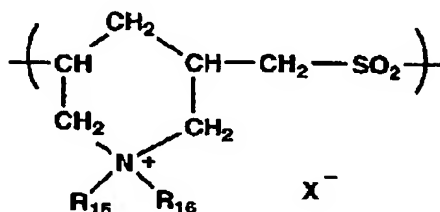
一般式(A-7)



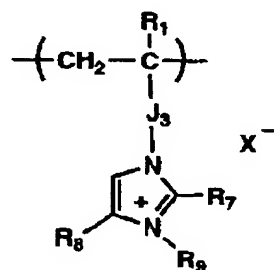
一般式(A-3)



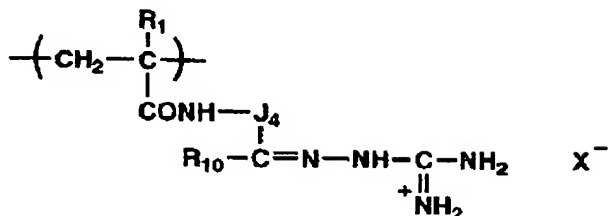
一般式(A-8)



一般式(A-4)



一般式(A-5)



[0065] In a general formula (A-1), R1 expresses the alkyl group of a hydrogen atom or the carbon atomic numbers 1-4. J1 expresses a divalent connection radical and expresses the benzyl which is not permuted [a methylene group, a permutation, or] or -COY-. A carbon atom is the divalent connection radical of 1-20, for example, Y expresses an alkylene group, an arylene radical, and a -O-Y'- radical and -NH-Y'-radical (Y' is an alkylene group, an arylene radical, an aralkylene group, etc.). R2 may express the alkyl group of a hydrogen atom or the carbon atomic numbers 1-18, or the aralkyl radical of the carbon atomic numbers 7-18, and these alkyl groups or an aralkyl radical may have a substituent. R3 and R4 may express the alkyl group of the carbon atomic numbers 1-18, or the aralkyl radical of the carbon atomic numbers 7-18 respectively, and these alkyl groups or an aralkyl radical may have a substituent. X- expresses an anion, for example, expresses halogen ion, alkyl sulfonic-acid ion, aryl sulfonic-acid ion, acetic-acid ion, etc.

[0066] In a general formula (A-2), R' expresses the alkyl group of a hydrogen atom or the carbon atomic numbers 1-18, or the aralkyl radical of the carbon atomic numbers 7-18.

[0067] a general formula (A-3) — and (A-4) it sets and J2 and J3 express a mere joint hand or divalent connection radicals (an alkylene group, an arylene radical, aralkylene group, etc.). R1 and X- are synonymous

with R1 of a general formula (A-1), and X-. R5-R8 express a hydrogen atom, an alkyl group, or an aralkyl radical independently, respectively. R9 expresses an alkyl group or an aralkyl radical.

[0068] In a general formula (A-5), R1 and X- are synonymous with R1 of a general formula (A-1), and X-. R10 expresses an alkyl group.

[0069] In a general formula (A-6), (A-7), and (A-8), R11, R12, R13, R14, R15, and R16 may express the alkyl group of a hydrogen atom or the carbon atomic numbers 1-18, or the aralkyl radical of the carbon atomic numbers 7-18 independently, respectively, and these alkyl groups or an aralkyl radical may have the substituent. X- is synonymous with X- of a general formula (A-1).

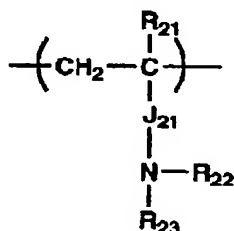
[0070] A general formula (A-1) is used especially more preferably still also in this.

[0071] (B) expresses the repeat unit guided from the monomer chosen from the following general formula (B-1) and acrylamide, methacrylamide, N,N-dimethylacrylamide, N-isopropyl acrylamide, diacetone acrylamide, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, and N-vinyl pyrrolidone among a general formula (L).

[0072]

[Formula 2]

一般式(B-1)



[0073] R21 expresses the alkyl group of a hydrogen atom or the carbon atomic numbers 1-4 among a formula. J21 expresses a divalent connection radical and expresses the benzyl which is not permuted [a methylene group, a permutation, or] or -COY-. A carbon atom is the divalent connection radical of 1-20, for example, Y expresses an alkylene group, an arylene radical, and a -O-Y'- radical and -NH-Y'-radical (Y' is an alkylene group, an arylene radical, an aralkylene group, etc.). R22 and R23 may express the alkyl group of the carbon atomic numbers 1-18, or the aralkyl radical of the carbon atomic numbers 7-18 respectively, and these alkyl groups or an aralkyl radical may have a substituent.

[0074] (C) expresses the repeat unit guided from the monomer which has ethylene nature partial saturation radicals other than (A) and (B), and which can be copolymerized among a general formula (L). As such a monomer, styrene and its derivative, acrylic ester, methacrylic ester, an acrylic acid, a methacrylic acid, a koro ton acid, a maleic acid, an itaconic acid, a fumaric acid, vinyl pyrrolidone, and vinyl ether are mentioned, and two or more of sorts of this may be used, for example.

[0075] Y expresses and, as for Z, X expresses 0 - 70-mol % 0 - 60-mol% 10 - 70-mol% among a general formula (L). However, when using two or more sorts of (C), Z expresses mol % of the sum total.

[0076] It is desirable especially desirable that it is 0.3:1-3:1 in a weight ratio, and the water-soluble cationic polymer used for this invention and a hydrophilic binder are 0.5:1-2:1. If larger [if the ratio of a water-soluble cation polymer is smaller than this ratio, the water resisting property of coloring matter and **-proof are inadequate, and] than this ratio, the absorptivity of ink will worsen and print image quality will deteriorate.

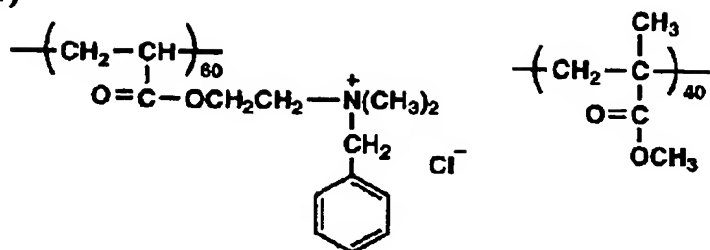
[0077] The water-soluble cationic polymer used for this invention may need to contain in the layer of the side which is most separated from a base material at least among the two-layer ink absorbing layers prepared on the base material, and it may contain it in layers other than this further. When it does not contain in the layer of the side which is most separated from a base material but contains only in the layer of the side near a base material, the water resisting property of coloring matter is inadequate, and it is not desirable.

[0078] Although the example of the cationic polymer used for this invention is shown below, it is not limited to this.

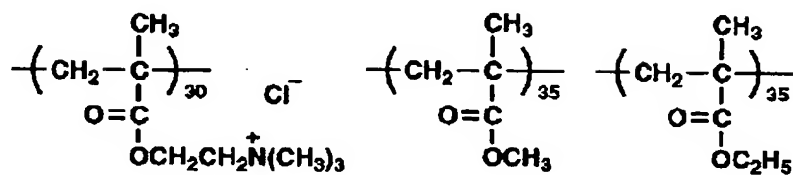
[0079]

[Formula 3]

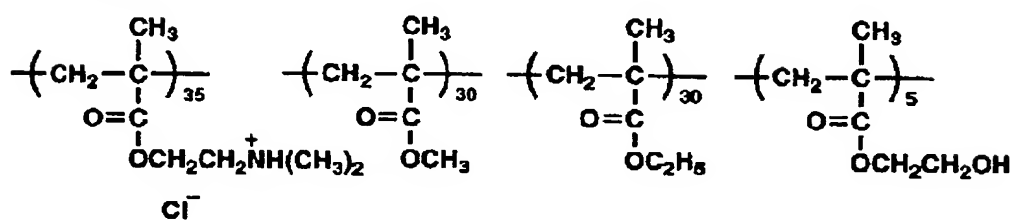
(C-1)



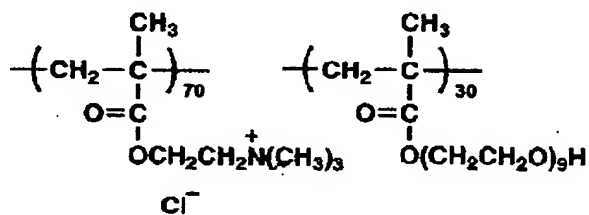
(C-2)



(C-3)



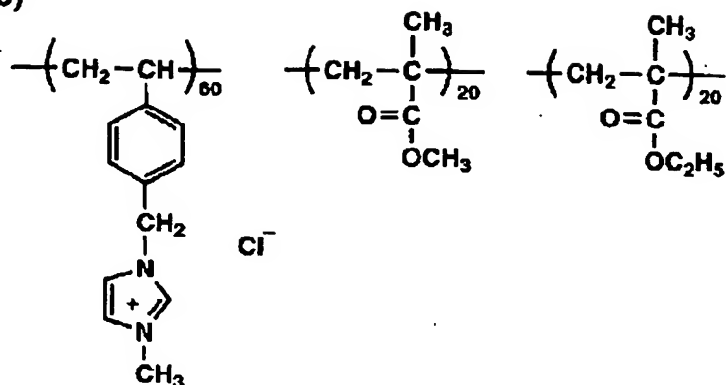
(C-4)



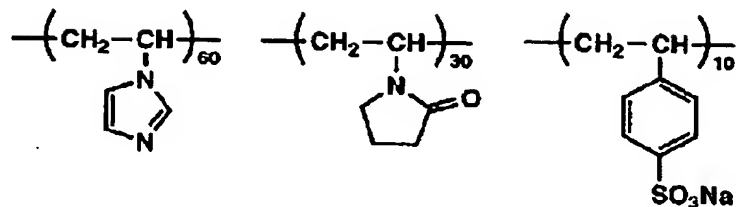
[0080]

[Formula 4]

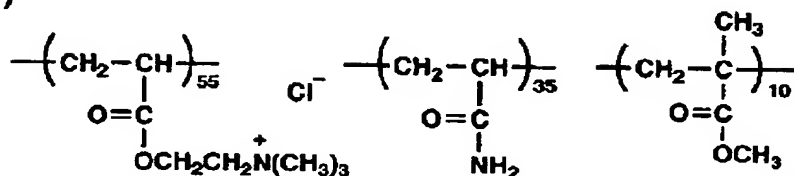
(C-5)



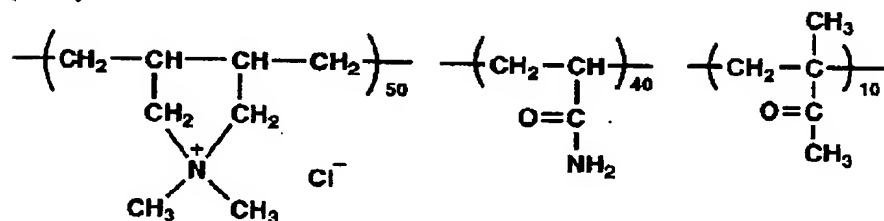
(C-6)



(C-7)



(C-8)



[0081] As for the ink jet record form of this invention, it is desirable to make at least one sort chosen from the compound which absorbs an image stabilizer and ultraviolet rays as a fading inhibitor in order to raise the lightfastness of water soluble dye contain. A water-soluble thing may be chosen and you may mix to coating liquid, and an image stabilizer may carry out oil distribution of the oil solubility thing, may make it an oil droplet, and may be mixed to coating liquid.

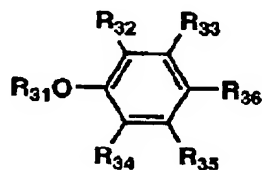
[0082] The fading inhibitor the image stabilizer used for this invention is indicated to be by JP,57-74192,A, 57-87989, 60-72785, 61-146591, JP,1-95091,A, 3-13376, etc. is mentioned.

[0083] As a desirable image stabilizer, a general formula (ST-I) and (ST-II) the compound expressed are mentioned.

[0084]

[Formula 5]

一般式(ST-I)



[0085] R₃₁ expresses a hydrogen atom, an alkyl group, an alkenyl radical, or an aryl group among a formula, and R₃₂, R₃₃, R₃₄, R₃₅, and R₃₆ express a hydrogen atom, a halogen atom, a cyano group, a nitro group, hydroxyl, a sulfonic group, or a univalent organic radical respectively.

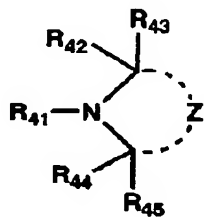
[0086] However, when R31 is a hydrogen atom, R32 and R34 are not hydrogen atoms at coincidence. Moreover, when R31 is an alkyl group, an alkenyl radical, or an aryl group, as for at least one of R32, R33, R34, R35, and the R36, -OR37 (R37 is an alkyl group or an alkenyl radical) or -N (R38)R39, (R38, and R39 are hydrogen atom, alkyl group, or alkenyl radical) respectively.

[0087] Respectively, it may join together mutually and R31, R32 and R32, R33 and R33, R36 and R36, R35 and R35, and R34, R34 and R31 may form a ring.

[0088]

[Formula 6]

一般式(ST-II)



[0089] R41 expresses a hydrogen atom, an alkyl group, an alkenyl radical, a phenyl group, hydroxyl, a sulfonyl group, a sulfinyl group, or an acyl group among a formula, and R42, R43, R44, and R45 express a hydrogen atom or an alkyl group respectively. Z expresses a nonmetal atom group required to form the nitrogen-containing heterocycle of 5 - 7 member.

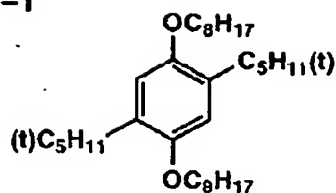
[0090] Respectively, it may join together mutually and R41, R42 and R42, R43 and R44, and R45, R44 and R41 may form a ring.

[0091] The example of the especially desirable image stabilizer used for this invention is shown below.

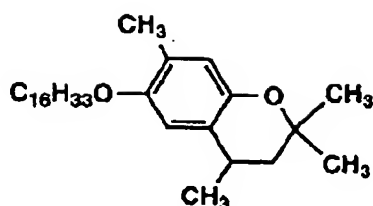
[0092]

[Formula 7]

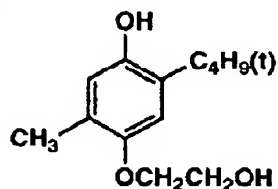
ST-1



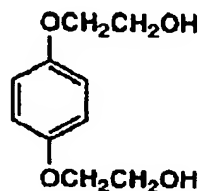
ST-2



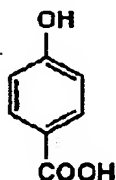
ST-3



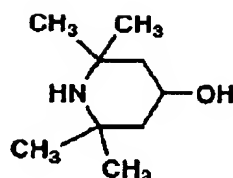
ST-4



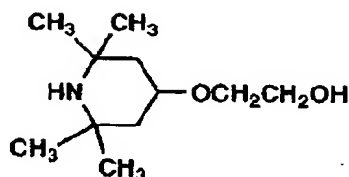
ST-5



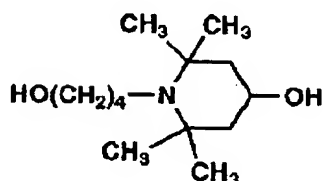
ST-6



ST-7



ST-8



[0093] The ink jet record form of this invention can make the compound which absorbs ultraviolet rays in order to raise the lightfastness of water soluble dye contain. As a compound which absorbs ultraviolet rays, the ultraviolet ray absorbent of a publication is mentioned, for example to JP,57-74193,A, 57-87988, 62-261476, etc. In order to make it ultraviolet rays not reach the water soluble dye which exists in a mordant layer, it is effective to see these ultraviolet ray absorbents from a base material rather than a mordant layer, and to make a far layer contain.

[0094] The amount of the above and the fading inhibitor used has desirable 0.01 - 5 g/m², and its 0.1 - 2 g/m² is still more desirable.

[0095] Various kinds of additives can be made to contain if needed in the ink receptiveness layer of the arbitration of the ink jet record form of this invention. For example, various well-known additives, such as pH regulators, such as the fluorescent brightener indicated by the well-known surfactant, JP,59-42993,A, a 59-52689 official report, a 62-280069 official report, a 61-242871 official report, JP,4-219266,A, etc. of various kinds, such as an anion, a cation, or Nonion, a sulfuric acid, a phosphoric acid, a citric acid, a sodium hydroxide, a potassium hydroxide, and potassium carbonate, a defoaming agent, antiseptics, a thickener, a hardening agent, an antistatic agent, and a mat agent, can also be made to contain.

[0096] In order to obtain without degrading the brittleness of the coat of high voidage, it is desirable that the dura mater of said hydrophilic binder is carried out by the hardening agent. Generally, a hardening agent is the compound which promotes the reaction of different radicals which said hydrophilic binder, the compound which has the radical which can react, or a hydrophilic binder has, according to the class of hydrophilic binder, is

chosen suitably and used. as the example of a hardening agent — for example, an epoxy system hardening agent (diglycidyl ethyl ether —) Ethylene glycol diglycidyl ether, 1,4-butanediol diglycidyl ether, A 1, 6-diglycidyl cyclohexane, N, and N-diglycidyl-4-glycidyoxy aniline, aldehyde system hardening agents (formaldehyde —), such as sorbitol polyglycidyl ether activity halogen system hardening agent [, such as glyoxal,], (2, and 4-dichloro-4-hydroxy - 1, 3, and 5-s-triazine etc. —) — An activity vinyl system compound, way acids (1, 3, 5-tris acryloyl-hexahydro-s-triazine, bisvinyl-sulfonyl methylether, etc.) and the salt of those, way sand, aluminum alum, etc. are mentioned.

[0097] As an especially desirable hydrophilic binder, when using polyvinyl alcohol and its derivative, it is the hardening agent chosen from a boric acid and its salt. By this invention, as a boric acid or its salt, the oxygen acid which uses a boron atom as a neutral atom, and its salt are shown, and orthoboric acid, 2 boric acids, metaboric acid, the tetraboric acid, 5 boric acids, 8 boric acids, and those salts are specifically contained.

[0098] Although the amount of the above-mentioned hardening agent used changes by the ratio to the class of hydrophilic binder, the class of hardening agent, the class of non-subtlety particle, and a hydrophilic binder etc., it is 5-100mg preferably 1-200mg per hydrophilic binder 1g in general.

[0099] The above-mentioned hardening agent may be added in the coating liquid which forms the layer of others which reach among the coating liquid of the opening stratification, or adjoin an opening layer in case the coating liquid which constitutes an opening layer is applied. Or although carrying out the overcoat of the hardening agent solution etc. can carry out hardening agent the coating liquid of not containing [which applies the coating liquid which forms said opening layer on the base material which has applied the coating liquid which contains a hardening agent beforehand, or forms an opening layer further], after spreading desiccation and a hardening agent can be supplied to an opening layer It is desirable to supply a hardening agent to to add a hardening agent and to form an opening layer into the coating liquid of the layer which adjoins the coating liquid or this which forms an opening layer from the effectiveness on manufacture preferably, and coincidence.

[0100] Although it is desirable to contain various drops in order to improve the brittleness of the coat of the ink absorption layer of the ink jet record form of this invention, the solubility over the water in a room temperature can make about 0.01 or less % of the weight of hydrophobic high-boiling point organic solvents (a liquid paraffin, dioctyl phthalate, tricresyl phosphate, silicone oil, etc.) and a polymer particle (particle to which the one or more sort polymerization of the monomers, such as styrene, butyl acrylate, a divinylbenzene, butyl methacrylate, and hydroxyethyl methacrylate, was carried out) contain as such an oil droplet. Such an oil droplet can be preferably used ten to 50% of the weight to a hydrophilic binder. It is also desirable that molecular weight contains 300 or less polyols to the brittleness of a coat. As such polyols, ethylene glycol, a diethylene glycol, triethylene glycol, tetraethylene glycol, a polo pyrene glycol, a glycerol, 1,6-hexanediol, 1, 2-cyclohexane diol, a with a molecular weight of 300 or less polyethylene glycol, or a polyethylene glycol is mentioned.

[0101] As a base material of the ink jet record form of this invention, a thing well-known as a record form for ink jets can be used suitably conventionally.

[0102] The thing of a property which bears the radiant heat when being able to mention the film which consists of ingredients, such as polyester system resin, diacetate system resin, triacetate system resin, acrylic resin, polycarbonate system resin, polyvinyl chloride system resin, polyimide system resin, cellophane, and celluloid, a plate, a glass plate, etc. as a transparence base material, for example, and being used as an OHP also in this is desirable, and especially polyethylene terephthalate is desirable. As thickness of such a transparent base material, about 10-200 micrometers is desirable.

[0103] Moreover, although what carried out opacification processing of the sheet which consists of common paper, a synthetic paper, resin covering paper, cloth, wood, a metal, etc. as a base material to be used, for example, a plate, and the above-mentioned translucency base material with the well-known means can be mentioned when there is no transparent need The so-called White pet which comes to add white pigments to the resin covering paper (the so-called RC paper) which has the polyolefin resin enveloping layer which added white pigments etc. at least to one side of a base paper, and polyethylene terephthalate is desirable. It is desirable to perform corona discharge treatment, undercoating processing, etc. to a base material in advance of spreading of an ink absorbing layer for the purpose, such as to enlarge bond strength of a base material and an ink television layer. Furthermore, the record form of this invention does not necessarily need to be colorlessness, and may be a colored record form.

[0104] Although it can carry out by choosing suitably the approach of applying the layer containing the non-subtlety particle of this invention on a base material from a well-known approach, the extrusion coat method which uses a hopper the roll coat method, the rod bar coat method, the air knife coat method, a spray coating method, the curtain coat method, or given in U.S. Pat. No. 2681294 is used preferably.

[0105] Moreover, after it cools and the gel state takes after applying on a base material as indicated by JP,6-64306,A in using the hydrophilic binder in which sol gel transformation, such as gelatin, and a gelatin derivative, a kappa carrageenan, is possible, you may carry out by the approach of drying by the cold dry cleaning method.

[0106] In case image recording is carried out using the ink jet record form of this invention, the record approach

which used water color ink is used.

[0107] The water color ink said by this invention is the following coloring agent and a solvent object, and a record liquid that consists of other additives. Water soluble dye, such as direct dye well-known as a coloring agent at an ink jet, acid dye, basic dye, reactive dye, or a food dye, can be used.

[0108] As a solvent of water color ink, water and water-soluble, various organic solvents For example, methyl alcohol, isopropyl alcohol, n-butyl alcohol, Alcohols, such as tert-butyl alcohol and isobutyl alcohol; Dimethylformamide, Amides, such as dimethylacetamide; Ketones, such as an acetone and diacetone alcohol, or a ketone-alcohol; tetrahydrofuran, Ether, such as dioxane; Polyalkylene glycols; ethylene glycol, such as a polyethylene glycol and a polypropylene glycol, Propylene glycol, a butylene glycol, triethylene glycol, 1, 2, 6-hexane triol, thiodiglycol, hexylene glycol, Polyhydric alcohol, such as a diethylene glycol, a glycerol, and triethanolamine; Ethylene glycol methyl ether, The low-grade alkyl ether of polyhydric alcohol, such as the diethylene-glycol methyl (or ethyl) ether and the triethylene glycol monobutyl ether, is mentioned.

[0109] Also in the water-soluble organic solvent of these many, the low-grade alkyl ether of the polyhydric alcohol of polyhydric alcohol, such as a diethylene glycol, triethanolamine, and a glycerol, and the triethylene glycol monobutyl ether etc. is desirable.

[0110] As an additive of other water color ink, a pH regulator, a sequestering agent, an antifungal agent, a viscosity controlling agent, a surface tension regulator, a wetting agent, a surfactant, a rust-proofer, etc. are mentioned, for example.

[0111] In order to make wettability to a record form good, as for water-color-ink liquid, in 20 degrees C, it is desirable to have the surface tension of 30 - 50 dyn/cm within the limits preferably 25 to 60 dyn/cm.

[0112] the ink jet recording method in which the regurgitation [water color ink] of the ink regurgitation method at the time of carrying out image recording using the ink jet record form of this invention is possible — it is — ***ing — for example, "ink jet record technical trend" Nakamura [Koichi] editing — recording methods, such as a continuation injection electric charge control system, a method on demand, etc. of a publication, can be used for work (Japanese Science-information, 1995) p.1-14. However, bigger effectiveness can be acquired by using it also in these, applying to the recording method of a method on demand.

[Translation done.]

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EXAMPLE

[Example] Although the example of this invention is given and explained below, this invention is not limited to these examples. In addition, in an example, "%", as long as there is no notice especially, oven-dry-weight % is shown, and an addition shows the amount per two 1m of ink jet record forms respectively.

[0114] The paper base material which covered stencil paper both sides of example 1100 g/m² with polyethylene (it is 7% of the weight of anatase mold titanium-dioxide content in the polyethylene layer by the side of 140 micrometers in thickness, and a recording surface.) In [having the layer which contains alkali treatment gelatin 1.2 g/m² and a hardening agent as a back layer in the rear-face side of a recording surface], coincidence multistory spreading desiccation was respectively performed for coating liquid -2 to the recording surface side by 100 micrometers of humid thickness as coating liquid -1 and the upper layer, and the record form 1 was obtained. The void volume of this coat was about 25 ml/m².

[0115]

[Coating liquid -1]

Pure water 1000ml Particle silica with a mean particle diameter of about 7nm 150g Polyvinyl alcohol of average degree of polymerization 3500 (5% water solution)

(Whenever [saponification] 89%) 500g (it indicates to Table 1) Cationic polymer (it indicates to Table 1) surfactant -3 1.2g Borax (4% water solution) the 20ml above-mentioned liquid — a high-speed homogenizer — distributing — white — translucent coating liquid was obtained.

[0116]

[Coating liquid -2]

Pure water 1000ml Particle silica with a mean particle diameter of about 7nm 150g Polyvinyl alcohol of average degree of polymerization 3500 (5% water solution)

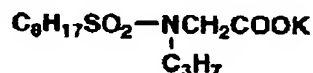
(Whenever [saponification] 89%) 500g (it indicates to Table 1) Cationic polymer (it indicates to Table 1)

Surfactant -1 0.70g Surfactant -2 0.30g Borax (4% water solution) The structure of the compound used by 20ml above is shown below.

[0117]

[Formula 8]

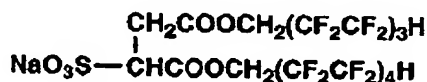
界面活性剤-1



界面活性剤-2



界面活性剤-3



[0118] The high-speed homogenizer distributed the above-mentioned liquid, and translucent white coating liquid was obtained.

[0119] As shown in Table 1, the weight ratio of addition, a cation polymer, and all polyvinyl alcohol was changed

for the primary particle diameter of the silica to be used, the water-soluble cation polymer, and the fading inhibitor, and also the record forms 2-19 as well as the record form 1 were created. Both the desiccation thickness and void volume of a record form that were done were also shown in Table 1.

[0120]

[Table 1]

記録用紙	第 1 層		第 2 層		全 層	
	シリカ 1 次粒子径 (nm)	カチオン 性ポリマ ー	カチオン 性ポリマ ー	退色防 止剤	カチオン性ポ リマー／P V A (重量比)	空隙容量 ml/m ²
1 (本発明)	7	—	C-2	—	0.7	25.0
2 (本発明)	7	—	C-6	—	0.7	24.1
3 (本発明)	7	—	C-7	—	0.7	24.5
4 (本発明)	7	C-2 *	C-2 *	—	0.7	24.8
5 (本発明)	7	—	C-2	—	0.2	25.7
6 (本発明)	7	—	C-2	—	0.5	25.3
7 (本発明)	7	—	C-2	—	2	23.8
8 (本発明)	7	—	C-2	—	3	23.0
9 (本発明)	7	—	C-2	—	4	21.5
10 (本発明)	7	—	C-6	①	0.7	23.8
11 (本発明)	7	—	C-6	②	0.7	23.7
12 (本発明)	7	—	C-6	③	0.7	23.3
13 (本発明)	12	—	C-7	—	0.7	24.1
14 (本発明)	20	—	C-7	—	0.7	23.1
15 (比較例)	40	—	C-7	—	0.7	20.5
16 (本発明)	7	—	I	—	0.7	25.2
17 (比較例)	7	C-2	—	—	0.7	24.7
18 (比較例)	7	—	II	—	0.7	19.8
19 (比較例)	7	—	—	—	0.7	19.8

[0121] *: the record form 4 divided the cationic polymer into the 1st layer and the 2nd layer ana, and added.

[0122] **: the record form 10 added 40ml (distributed object -1) of following.

[0123] **: the record form 11 added instantiation compound ST-4 [10g].

[0124] **: the record form 12 added instantiation compound ST-5 [10g].

[0125] (Distributed object -1) The solution 1 and solution 2 of the following presentation were prepared, and it mixed, and distributed in the ultrasonic disperser.

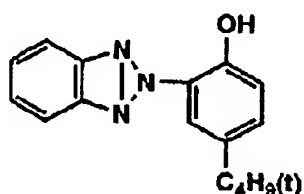
[0126]

Solution 1 Ultraviolet ray absorbent -1 1g G i-DESHIRU phthalate 1g Ethyl acetate 5ml solution 2 Gelatin 0.5g Surfactant -4 (tree i-propyl naphthalene sulfo N acid sodium) 0.2g Pure water Structure of the compound used by 15ml above It is shown below.

[0127]

[Formula 9]

紫外線吸収剤-1



[0128] About each obtained ink jet record form, using ink jet printer MJ[by Seiko Epson, Inc.]-900C, the evaluation pattern was printed and the following items were evaluated.

[0129] (1) Homogeneity was made to breathe out and it recorded so that it might become 30% of the amount of the maximum ink, respectively, and 20 red-reflex concentration of the solid section was measured using the

microdensitometer (aperture =200micrometerphi), and the value of ink absorptivity yellow and cyanogen broken by average reflection density in quest of the standard deviation of the variation in the concentration was calculated.

[0130] When ink absorptivity is good, the value of non-Lycium chinense becomes [nonuniformity] small at an image, but if ink absorptivity falls, this each other liquid ink drops will cause beading mutually in the record paper, it will become nonuniformity, and this value will increase.

[0131] (2) Visual evaluation of neglect and the imprint degree of the ink to a rear face was carried out on the following criteria for 1 minute, having applied the rear face of after [of an after / printing] 5 minutes, and a record form, and the load of superposition and 120 g/cm2 for 60% printing section of drying yellow and a Magenta.

[0132]

O : — completely — imprint-less O: — although imprinted slightly — a printing image — almost — effect-less
 x: — after a lot of ink carried out the dipping of the effect size (3) water-resisting-property printing sample to the imprint and the printing image for 10 minutes underwater [20-degree C], it dried and residual concentration compared the water resisting property of the printing image of the maximum-density part of a Magenta. It evaluated in four steps of OO**x from what has high concentration.

[0133] (4) The sample after damp-proof printing was saved for three days after two-week preservation and by 60-degree-C80%RH by 23 degrees C and 20%RH, and the blot degree of each color was evaluated. evaluation —
 O: — completely — blot-less O:blot width of face — less than (a blot is accepted slightly visually) about 0.1mm
 **: Blot width of face is 0.1mm – less than (permission is visually impossible) 0.5mm.

x: More than 0.5mm (with no value as an image)

(5) The sample of the maximum-density part of a light-fast Magenta was asked for the reflection density ratio before 20-hour Mitsuteru putting, and an exposure after an exposure in xenon fade meter.

[0134] (6) Gloss was measured for the glossiness printing side 60 degrees using the deflection glossmeter (VGS-1001DP) by Nippon Denshoku Industries Co., Ltd.

[0135] The obtained result is shown in Table 2.

[0136]

[Table 2]

記録用紙	インク吸収性	乾燥性	耐水性	耐湿性	耐光性	光沢度 (%)
1 (本発明)	0.10	○	○	○	75	57
2 (本発明)	0.10	○	○	○	70	50
3 (本発明)	0.10	○	○	○	70	51
4 (本発明)	0.10	○	◎	◎	70	55
5 (本発明)	0.08	◎	△	△	80	65
6 (本発明)	0.09	○	○	○	75	60
7 (本発明)	0.12	○	◎	○	70	50
8 (本発明)	0.13	○	◎	○	65	47
9 (本発明)	0.14	△	◎	◎	65	40
10 (本発明)	0.10	○	○	○	90	50
11 (本発明)	0.10	○	○	○	92	51
12 (本発明)	0.10	○	○	○	95	50
13 (本発明)	0.10	○	○	○	75	51
14 (本発明)	0.11	○	○	○	70	47
15 (比較例)	0.18	△	○	○	70	29
16 (本発明)	0.10	○	△	○	70	49
17 (比較例)	0.10	○	△	×	80	60
18 (比較例)	0.17	△	○	△	60	52
19 (比較例)	0.09	◎	×	×	70	65

[0137] Table 2 shows that the ink jet record form of this invention has good ink absorptivity, drying, a water resisting property, moisture resistance, lightfastness, and glossiness.

[0138] Glossiness falls greatly and, as for the record form 17 which added the cationic polymer only in the lower

layer, the record form 18 which added the cation polymer which is not water solubility, and the record form 19 which has not added the cationic polymer, a water resisting property and moisture resistance fall [the record form 15 using a silica with a large primary particle size] greatly.

[0139] Although it was opaque and the case where a glossy paper base material was used was explained by this example, the suitable ink jet record form for the application using transparency of CFM used for color displays, such as what observes a record image by projection to a screen etc., and the color-separation version at the time of creating the positive version of color printing or liquid crystal, by optical instruments, such as a slide and OHP, can be offered by using a base material with translucency.

[0140] Moreover, although the case where it mainly uses for an ink jet method has been explained about the record sheet of this invention, it can use suitable for record by record devices, such as various writing materials, a pen plotter, etc. which use water color ink besides an ink jet method.

[Translation done.]

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(54)【発明の名称】 インクジェット記録用紙

(57)【要約】

【課題】 水性インクによる印字において、高い光沢性を維持しつつ、しかも高いインク吸収性を有し、かつ、耐水性、耐湿性、耐光性の優れた高品位の画像を形成記録することができるインクジェット記録用紙の提供。

【解決手段】 支持体及びその上に設けられた少なくとも2層のインク受容層を有するインクジェット記録用紙において、該インク受容層が平均1次粒子径20nm以下のシリカ系微粒子と親水性バインダーを含有し、かつ少なくともインク受容層側の支持体から最も離れた層に水溶性カチオン性ポリマーを含有することを特徴とするインクジェット記録用紙。

【特許請求の範囲】

【請求項1】 支持体及びその上に設けられた少なくとも2層のインク受容層を有するインクジェット記録用紙において、該インク受容層が平均1次粒子径20nm以下のシリカ系微粒子と親水性バインダーを含有し、かつ少なくともインク受容層側の支持体から最も離れた層に水溶性カチオン性ポリマーを含有することを特徴とするインクジェット記録用紙。

【請求項2】 前記親水性バインダーがポリビニルアルコール及びその誘導体から選ばれる少なくとも1つであることを特徴とする請求項1記載のインクジェット記録用紙。

【請求項3】 前記水溶性カチオン性ポリマーと親水性バインダーが重量比で0.3:1~3:1であることを特徴とする請求項1または2記載のインクジェット記録用紙。

【請求項4】 全てのインク受容層が前記水溶性カチオン性ポリマーを含有することを特徴とする請求項1~3の何れか1項記載のインクジェット記録用紙。

【請求項5】 退色防止剤として画像安定剤及び紫外線を吸収する化合物から選ばれる少なくとも1種を含有することを特徴とする請求項1~4の何れか1項記載のインクジェット記録用紙。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、水性インクを用いて記録を行うインクジェット記録用紙に関し、詳しくは光沢性、インク吸収性、耐水性、耐湿性、耐光性を改善したインクジェット記録用紙に関するものである。

【0002】

【従来の技術】インクジェット記録は、インクの微小液滴を種々の作動原理により飛翔させて紙などの記録シートに付着させ、画像・文字などの記録を行うものであるが、比較的高速、低騒音、多色化が容易である等の利点を有している。この方式で従来から問題となっていたノズルの目詰まりとメンテナンスについては、インクおよび装置の両面から改良が進み、現在では各種プリンター、ファクシミリ、コンピューター端末等、さまざまな分野に急速に普及している。

【0003】このインクジェット記録方式で使用される記録用紙としては、印字ドットの濃度が高く、色調が明るく鮮やかであること、インクの吸収が早く印字ドットが重なった場合に於いてもインクが流れ出したり滲んだりしないこと、印字ドットの横方向への拡散が必要以上に大きくなく、かつ周辺が滑らかでぼやけないこと等が要求される。

【0004】特にインク吸収速度が遅い場合には、2色以上のインク液滴が重なって記録される際に、記録用紙上で液滴がハジキ現象を起こしてムラになったり、また、異なる色の境界領域でお互いの色が滲んだりして画

質を大きく低下させやすいために、記録用紙としては高いインク吸収性を持たせるようにすることが必要である。

【0005】これらの問題を解決するために、従来から非常に多くの技術が提案されている。

【0006】例えば、特開昭52-53012号公報に記載されている低サイズ原紙に表面加工用の塗料を湿潤させた記録用紙、特開昭55-5830号に記載されている支持体表面にインク吸収性の塗層を設けた記録用紙、特開昭56-157号公報に記載されている被履層中の顔料として非膠質シリカ粉末を含有する記録用紙、特開昭57-107878号に記載されている無機顔料と有機顔料を併用した記録用紙、特開昭58-110287号公報に記載されている2つの空孔分布ピークを有する記録用紙、特開昭62-111782号に記載されている上下2層の多孔質層からなる記録用紙、特開昭59-68292号、同59-123696号および同60-18383号公報などに記載されている不定形亀裂を有する記録用紙、特開昭61-135786号、同61-148092号および同62-149475号公報等に記載されている微粉末層を有する記録用紙、特開昭63-252779号、特開平1-108083号、同2-136279号、同3-65376号および同3-27976号等に記載されている特定の物性値を有する顔料や微粒子シリカを含有する記録用紙、特開昭57-14091号、同60-219083号、同60-210984号、同61-20797号、同61-188183号、特開平5-278324号、同6-92011号、同6-183134号、同7-137431号、同7-276789号等に記載されているコロイド状シリカ等の微粒子シリカを含有する記録用紙、および特開平2-276671号、同3-67684号、同3-215082号、同3-251488号、同4-67986号、同4-263983号および同5-16517号公報などに記載されているアルミナ水和物微粒子を含有する記録用紙等が多数知られている。

【0007】しかし、インク受容層がインクを吸収したり保持するための空隙を多く有する層のみから構成される場合、空隙の多いインク受容層が空気との界面や皮膚表面のミクロな凹凸を多く有することになり、インク受容層への入射光が散乱されたり、透過が妨げられるために、光沢が出にくくなったり不透明になりやすい。

【0008】また、空隙を形成するため顔料自身の凹凸や顔料の2次凝集体の凹凸による皮膚表面の平滑性が低下して光沢が出にくい欠点がある。

【0009】一方、皮膚中に空隙を設けることなくインク吸収層のバインダーの膨潤作用でインクを吸収、保持するタイプのインクジェット記録用紙も数多く知られている。

【0010】例えば、バインダーとしてゼラチン、カゼ

イン、澱粉、アルギン酸、ポリビニルアルコール、各種の変性ポリビニルアルコール、ポリビニルピロリドン、ポリエチレンオキサイド、ポリプロピレンオキサイド、カルボキシメチルセルロース、ヒドロキエチルセルロース、デキストラン、プルラン等の親水性バインダーを支持体上に塗布した記録紙やフィルム等も従来から数多く知られている。

【0011】これらの記録用紙はインク吸収性が上記空隙を有する記録用紙に比べて劣るものの高い光沢性や光学濃度、鮮明な画像が得られ高画質記録用途として有用である。

【0012】上記の水溶性インクに適した各種のインクジェット記録用紙においては、色素分子が油剤中に高濃度の微粒子状態で分散されているカラー印画紙等とは異なり、色素分子が単独でバインダー中や空隙間に存在するために、水滴が記録面にかかったり、印字後に高湿度条件下で長期間保存された際に滲んだり流れ出したりしやすい欠点があった。

【0013】この色素の耐水性や耐湿性を改良するために、従来から色素をバインダー中に固定させる種々の方法が提案されている。特に有効な手段は3級または4級の窒素原子を有するポリマーを均一な水溶液としてまたは微粒子ラテックスとして添加する方法である。

【0014】例えば特開昭57-36692号にはゼラチンをバインダーの一部とし塩基性媒染剤を含有する塗布液をインク受容層として原紙やポリエチレンテレフタレートフィルム支持体上に塗布したインクジェット記録用紙が記載されている。

【0015】特開昭53-49113号には、紙内にポリエチレンイミンを含浸させた水性インキ記録用紙が記載されている。

【0016】特開昭58-24492号にはカチオンまたはアニオン基を有する電解質ポリマーを有する記録材が記載されている。

【0017】特開昭63-224988号には、インク受容層内に第1級ないし第3級アミンまたは第4級アンモニウム塩を含有し、インク保持層のpHが2～8にある被記録材料が記載されている。

【0018】特開昭63-307979号には、3級または4級窒素原子を有する親水性ポリマー媒染剤と親水性基を有する重合体を含有する層を有するインクジェット記録用紙が記載されている。

【0019】特開昭59-198186号および同59-198188号にはポリエチレンイミンの有機塩基を基材中または基材上の塗工層中に含有させた記録材料が記載されている。

【0020】特開昭60-46288号には特定染料を含有するインクとポリアミン等を含有する記録材料を用いたインクジェット記録方法が記載されている。

【0021】特開昭61-61887号、同61-72

581号、同61-252189号および同62-174184号にはポリアリルアミンを含有するインクジェット記録用紙が記載されている。

【0022】特開昭61-172786号には分子間水素結合を有するポリマー（ゼラチン、ポリエチレニン等）と分子間に水素結合性基を有しないポリマー（ポリエチレングリコール、ポリビニルピロリドン等）を含有するインクジェット記録材料が記載されている。

【0023】特開昭63-162275号にはカチオン性ポリマーとカチオン性界面活性剤を支持体上に塗布または含浸させたインクジェット記録用紙が記載されている。

【0024】特開平6-143798号にはプラスチック支持体上に第4級アンモニウム塩重合体とカチオン変性ポリビニルアルコールを主成分とする染料定着層とその上に設けられた染料透過・インク吸収層を重畳した記録用紙が記載されている。

【0025】更に、特開昭59-20696号、同59-33176号、同59-33177号、同59-96987号、同59-155088号、同60-11389号、同60-49990号、同60-83882号、同60-109894号、同61-277484号、同61-293886号、同62-19483号、同62-198493号、同63-49478号、同63-115780号、同63-203896号、同63-274583号、同63-280681号、同63-260477号、特開平1-9776号、同1-20188号、同1-24784号、同1-40371号、同3-133686号、同6-234268号、同7-125411号等にはそれぞれ特定の3級または4級の窒素原子を含有するポリマーまたは化合物をインク受容層中に添加することが記載されている。

【0026】しかしながら、上記の従来の方法によれば色素の耐水性は向上するものの、耐光性が低下してしまうものが大半である。

【0027】またある種のポリマーはコストが高いという欠点があったり、使用するバインダーとの相溶性が低く良好な塗布ができないか、あるいは少量しか使用できない等の欠点があった。

【0028】特開平7-125412号にはバインダーとフィラーからなるインク吸収層に皮膜の耐水化剤を存在させ、該インク吸収層の表面及び／または表層内にインク染料の定着剤を局在させる記録シート及びその製造方法が記載されているが、インク吸収層に添加できない染料定着剤を吸収層にオーバーコートすることの特徴としており、塗布工程を2回通すことによるコストが高い欠点があった。

【0029】特開平5-124329号にはカチオン性ポリマー層上に顔料及び水溶性バインダー層のアニオン性層を、特開平5-131742号には4級アンモニウ

ム塩重合物を主成分とする染料定着層にインク吸収層を順次積層、特開平7-242056号は4級アンモニウム塩水溶性ポリマー含有吸収層にシリカ微粒子と特定量の水可溶アルコール不溶ポリマー含有層を設ける記録用紙が記載されているが、いずれもインク吸収性、色素耐水性とも十分とはいえなかった。

【0030】

【発明が解決しようとする課題】本発明は上記の実態に鑑みてなされたものであって、本発明の目的は、水性インクによる印字において、高い光沢性を維持しつつ、しかも高いインク吸収性を有し、かつ、耐水性、耐湿性、耐光性の優れた高品位の画像を形成記録することができるインクジェット記録用紙を提供することである。

【0031】

【課題を解決するための手段】本発明の上記目的は、下記構成により達成される。

【0032】(1) 支持体及びその上に設けられた少なくとも2層のインク受容層を有するインクジェット記録用紙において、該インク受容層が平均1次粒子径20nm以下のシリカ系微粒子と親水性バインダーを含有し、かつ少なくともインク受容層側の支持体から最も離れた層に水溶性カチオン性ポリマーを含有することを特徴とするインクジェット記録用紙。

【0033】(2) 前記親水性バインダーがポリビニルアルコール及びその誘導体から選ばれる少なくとも1つであることを特徴とする(1)記載のインクジェット記録用紙。

【0034】(3) 前記水溶性カチオン性ポリマーと親水性バインダーが重量比で0.3:1~3:1であることを特徴とする(1)または(2)記載のインクジェット記録用紙。

【0035】(4) 全てのインク受容層が前記水溶性カチオン性ポリマーを含有することを特徴とする(1)~(3)の何れか1項記載のインクジェット記録用紙。

【0036】(5) 退色防止剤として画像安定剤及び紫外線を吸収する化合物から選ばれる少なくとも1種を含有することを特徴とする(1)~(4)の何れか1項記載のインクジェット記録用紙。

【0037】以下、本発明を詳細に説明する。

【0038】本発明のインクジェット記録用紙は親水性のバインダーとシリカ系微粒子によって形成される空隙によって高いインク吸収性が得られる。

【0039】一般に固体微粒子と親水性バインダーによる代表的な空隙の形成方法としては以下のような方法が考えられる。

【0040】(1) 多孔質固体微粒子と親水性バインダーを含有する塗布液を支持体上に塗布し、多孔質微粒子内や粒子間に空隙を形成する方法

(2) 親水性バインダーに対して概ね等量以上(好ましくは10倍以上)の容積を有する固体微粒子と親水性バ

インダーを含有する塗布液を支持体上に塗布して固体微粒子の間に空隙を作成する方法

(3) 平均粒径が約0.1 μ m程度以下の固体微粒子を塗布液調製時または皮膜形成時に凝集させて2次粒子または3次元構造を形成して空隙を作成する方法。

【0041】一般に方法(1)は、インク吸収性に優れ、従来よりコート紙等で広く用いられているが、多孔質固体微粒子は合成不定形シリカに代表されるようにほとんどが2次凝集しているミクロンオーダーの粒子径の大きな粒子で、この方法で得られた空隙層だけでは十分な光沢性を得ることは困難であった。

【0042】前記方法(2)は、インク吸収性に優れるが、親水性バインダーに対して固体微粒子が高比率のため皮膜の脆弱化は避けられず、特にプラスチックフィルム等の非吸収性支持体を用いた場合、製造過程や使用の際、吸収層のヒビワレや粉落ち等の種々の問題がおこることがあった。

【0043】本発明において好ましい態様は、前記方法(3)である。この方法は固体微粒子で軟凝集状態を形成して網目構造を皮膜中に形成する方法で、好ましくは親水性ポリマーを含有する水溶液中に分散状態にある1次超微粒子が、接触点が比較的制限された状態で互いに凝集し合う状態を経由して形成される。このような軟凝集状態は直線的もしくは分岐状に凝集体を形成したものが水溶液中に分散された状態や、あるいはこれらの凝集体が更に凝集し合って水溶液中で3次元網目構造をとる状態が含まれる。いずれの場合であっても、この水溶液を支持体上に塗布乾燥することによって、形成された皮膜中に微細な構造を形成することが出来る。

【0044】この様にして得られた皮膜中の微細な空隙の大きさは、概ね1次粒子の大きさからそれらの数倍程度の大きさであり、微細な大きさの空隙である特徴がある。

【0045】この様な軟凝集状態を形成する方法としては、例えば1次粒子がお互いに凝集しにくく、安定に存在できるような親水性ポリマーを含有する水溶液中に、粒子の凝集を加速するような親水性ポリマーを極微量添加して僅かに凝集を形成する方法、あるいは1次粒子表面と弱い結合が出来るような水溶性ポリマーを有する水溶液中で形成される。

【0046】本発明では、特に、後者の方法が空隙の量を比較的コントロールしやすく安定に形成しやすいこと、使用する微粒子の量に比較してより多い空隙量が得られることから好ましく、さらには皮膜の光沢性がより高い皮膜が得られることから1次粒子の粒子径(平均1次粒子径)が20nm以下のシリカ微粒子を用いる。

【0047】本発明のインクジェット記録用紙に使用する親水性バインダーとしては、ゼラチンまたはゼラチン誘導体、ポリビニルピロリドン(平均分子量が約20万以上が好ましい)、プルラン、ポリビニルアルコールま

たはその誘導体（平均分子量が約2万以上が好ましい）、ポリエチレングリコール（平均分子量が10万以上が好ましい）、カルボキシメチルセルロース、ヒドロキシエチルセルロース、デキストラン、デキストリン、ポリアクリル酸およびその塩、アクリルアミド系ポリマー、寒天、κ-カラギーナン、λ-カラギーナン、ι-カラギーナン、キサンテンガム、ローカストビーンガム、アルギン酸、アラビアゴム、プルラン、特開平7-195826号および同7-9757号に記載のポリアルキレンオキサイド系共重合性ポリマー、水溶性ポリビニルブチラール、あるいは、特開昭62-245260号に記載のカルボキシル基やスルホン酸基を有するビニルモノマーの単独またはこれらのビニルモノマーを繰り返して有する共重合体等のポリマーを挙げることができる。これらの親水性バインダーは単独で使用しても良く、2種以上を併用しても良い。

【0048】本発明のインクジェット記録用紙において、好ましいのは平均1次粒子径が20nm以下の微粒子としてシリカ微粒子に対し、親水性バインダーとしてポリビニルアルコールまたは変性ポリビニルアルコールを用いる場合である。この場合、微粒子シリカ表面のシラノール基とビニルアルコールの水酸基が弱い水素結合を行い、前記軟凝集体が良好に形成される。

【0049】前記シリカ微粒子としては、特に6~15nmのものが最も好ましい。また、これらが連結した2次粒子としては20~200nm、好ましくは30~100nm程度になるようにするのが好ましい。

【0050】この様な微粒子シリカは、例えば特開昭60-204390号記載の通常気相法と呼ばれる合成方法で合成された微粒子シリカが好ましく用いられる。また、このシリカ微粒子は表面をシランカップリング剤のようなものでカチオン変性されたものであってもよく、また、Al、Ca、MgおよびBa等で処理された物であってよい。

【0051】本発明で好ましく用いられる親水性バインダーはポリビニルアルコールまたはその誘導体である。ポリビニルアルコールまたはその誘導体とは、完全または部分ケン化のポリビニルアルコールまたはカチオン変性ポリビニルアルコールである。ポリビニルアルコールの中でも特に好ましいのはケン化度が80以上の部分または完全ケン化したものである。また、皮膜脆弱性を改良する観点から、平均重合度は500~3500、特に好ましくは1000~3500のものが用いられる。

【0052】また、カチオン変性ポリビニルアルコールとしては、例えば特開昭61-10483号に記載されているような、第1~3級アミノ基や第4級アンモニウム基を上記ポリビニルアルコールの主鎖または側鎖中に有するポリビニルアルコールである。

【0053】この方法で、親水性バインダーとして特に好ましく用いられるポリビニルアルコールの重合度は1

000以上、特に1500以上が皮膜にひび割れを起こさないようにするために好ましい。

【0054】ここで、ポリビニルアルコールと上記シリカの比率は、概ね1:10~1:1であり、好ましくは1:7~1:2の範囲である。

【0055】ポリビニルアルコールと微粒子シリカを用いて軟凝集体を含有する皮膜を形成する方法について以下に簡単に説明する。

【0056】pHを6~8、温度約40℃に保ったポリビニルアルコール水溶液（概ね5~15%）中に、シリカ分散液（概ね5~15%）を強撹拌しながら徐々に添加し、添加終了後に超音波分散機や高速ホモジナイザーなどにより分散する。この場合均一な塗布液を調製するため、必要に応じて各種の界面活性剤やメタノール、アセトン等の水混和性有機溶媒を使用してもよい。ついで、各種の添加剤を添加後、塗布に必要な目標粘度に調整して支持体上に公知の方法で塗布し乾燥することで上記空隙を有する皮膜が得られる。

【0057】前記空隙層中には他の親水性バインダーを含有させることが出来るが、好ましくはそれらの親水性バインダーは前記ポリビニルアルコールまたはその誘導体に対して概ね20重量%以下であることが好ましい。

【0058】本発明のインクジェット記録用紙のインク吸収層には本発明の効果を損なわない範囲で固体微粒子として従来インクジェット記録用紙で公知の各種の無機または有機の固体微粒子を用いることが出来る。用いられる無機微粒子の例としては、軽質炭酸カルシウム、重質炭酸カルシウム、炭酸マグネシウム、カオリン、クレイ、タルク、硫酸カルシウム、硫酸バリウム、二酸化チタン、酸化亜鉛、水酸化亜鉛、硫化亜鉛、炭酸亜鉛、ハイドロタルサイト、珪酸アルミニウム、ケイソウ土、珪酸カルシウム、珪酸マグネシウム、合成非晶質シリカ、気相法シリカ、コロイダルシリカ、アルミナ、コロイダルアルミナ、擬ペーナイト、水酸化アルミニウム、リトポン、ゼオライト、水酸化マグネシウム等の白色無機顔料等を挙げることが出来る。

【0059】一方有機微粒子の例としては、ポリスチレン、ポリアクリル酸エステル類、ポリメタクリル酸エステル類、ポリアクリルアミド類、ポリエチレン、ポリプロピレン、ポリ塩化ビニル、ポリ塩化ビニリデン、またはこれらの共重合体、尿素樹脂、またはメラミン樹脂等が挙げられる。

【0060】本発明のインクジェット記録用紙においてインクの吸収性と色素の耐水性や耐湿性の両方を改良するための水溶性カチオン性ポリマーを用いる。

【0061】例えば特開昭57-36692号記載のような3級または4級の窒素原子を有するポリマーの微粒子ラテックスを添加する方法では、インクの吸収性を損なう場合があり、好ましくない。理由は明確ではないが、おそらく、ラテックス粒子が親水性バインダーとシ

リカ系微粒子による空隙形成をさまたげるためと推定される。本発明に使用される水溶性カチオンポリマーとしては、ポリエチレンイミン、特開昭59-20696号、同59-33176号、同59-33177号、同59-155088号、同60-11389号、同60-49990号、同60-83882号、同60-109894号、同62-198493号、同63-49478号、同63-115780号、同63-280681号、特開平1-40371号、同6-234268号、同7-125411号等に記載された1～3級アミ

ノ基、4級アンモニウム塩基を有するポリマーが好ましく用いられる。

【0062】これらのうち、特に好ましく用いられる水溶性ポリマーは下記一般式で表される。

【0063】一般式(L)

(A)_x-(B)_y-(C)_z

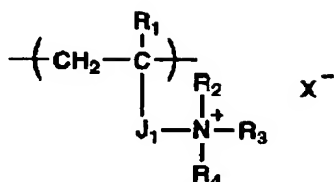
一般式(L)中、Aは下記一般式(A-1)～(A-8)で表される。

【0064】

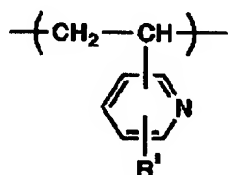
【化1】

11

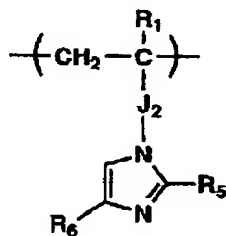
一般式(A-1)



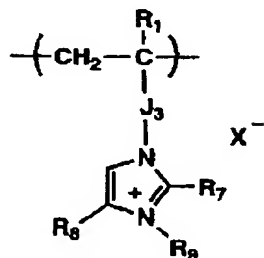
一般式(A-2)



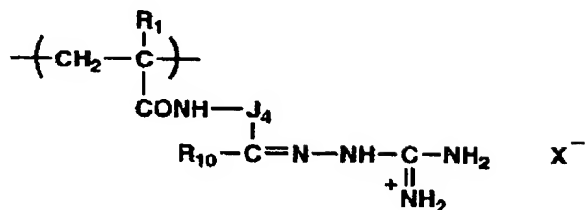
一般式(A-3)



一般式(A-4)

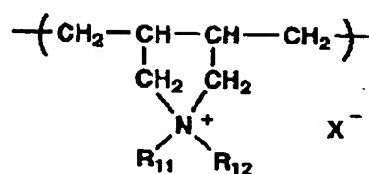


一般式(A-5)

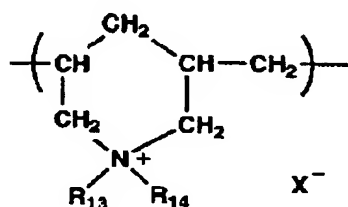


12

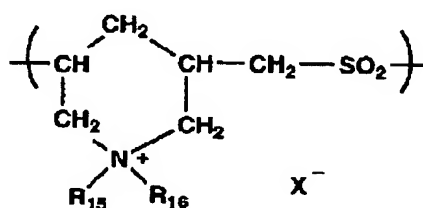
一般式(A-6)



一般式(A-7)



一般式(A-8)



【0065】一般式(A-1)において、R₁は水素原子または炭素原子数1~4のアルキル基を表す。J₁は2価の連結基を表し、メチレン基、置換または未置換のベンジル基または-COY-を表す。Yは炭素原子が1~20の2価の連結基であり、例えばアルキレン基、アリーレン基、-O-Y'-基、-NH-Y'-基(Y'はアルキレン基、アリーレン基、アラルキレン基等)を表す。R₂は水素原子または炭素原子数1~18のアルキル基または炭素原子数7~18のアラルキル基を表

し、これらのアルキル基またはアラルキル基は置換基を有してもよい。R₃及びR₄は各々、炭素原子数1~18のアルキル基または炭素原子数7~18のアラルキル基を表し、これらのアルキル基またはアラルキル基は置換基を有してもよい。X⁻は陰イオンを表し、例えばハロゲンイオン、アルキルスルホン酸イオン、アリールスルホン酸イオン、酢酸イオン等を表す。

【0066】一般式(A-2)においてR'は水素原子または炭素原子数1~18のアルキル基または炭素原子

数7～18のアラルキル基を表す。

【0067】一般式(A-3)及び(A-4)において、J₂及びJ₃は単なる結合手または2価の連結基(アルキレン基、アリーレン基、アラルキレン基等)を表す。R₁とX⁻は一般式(A-1)のR₁、X⁻と同義である。R₅～R₈はそれぞれ独立に水素原子、またはアルキル基またはアラルキル基を表す。R₉はアルキル基またはアラルキル基を表す。

【0068】一般式(A-5)においてR₁とX⁻は一般式(A-1)のR₁、X⁻と同義である。R₁₀はアルキル基を表す。

【0069】一般式(A-6)、(A-7)、(A-8)において、R₁₁、R₁₂、R₁₃、R₁₄、R₁₅、R₁₆はそれぞれ独立に水素原子または炭素原子数1～18のアルキル基または炭素原子数7～18のアラルキル基を表し、これらのアルキル基またはアラルキル基は置換基を有していてもよい。X⁻は一般式(A-1)のX⁻と同義である。

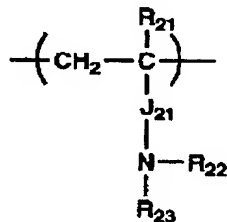
【0070】さらにこの中でも特に好ましく用いられるのは、一般式(A-1)である。

【0071】一般式(L)中、(B)は下記一般式(B-1)及びアクリルアミド、メタクリルアミド、N、N-ジメチルアクリルアミド、N-イソプロピルアクリルアミド、ジアセトンアクリルアミド、2-ヒドロキシエチル(メタ)アクリレート、2-ヒドロキシプロピル(メタ)アクリレート、N-ビニルピロリドンから選ばれるモノマーから誘導される繰り返し単位を表す。

【0072】

【化2】

一般式(B-1)



【0073】式中、R₂₁は水素原子または炭素原子数1

～4のアルキル基を表す。J₂₁は2価の連結基を表し、メチレン基、置換または未置換のベンジル基または-COY-を表す。Yは炭素原子が1～20の2価の連結基であり、例えばアルキレン基、アリーレン基、-O-Y'-基、-NH-Y'-基(Y'はアルキレン基、アリーレン基、アラルキレン基等)を表す。R₂₂及びR₂₃は各々、炭素原子数1～18のアルキル基または炭素原子数7～18のアラルキル基を表し、これらのアルキル基またはアラルキル基は置換基を有してもよい。

【0074】一般式(L)中、(C)は、(A)、

(B)以外のエチレン性不飽和基を有する共重合可能なモノマーから誘導される繰り返し単位を表す。このようなモノマーとしては、例えば、スチレン及びその誘導体、アクリル酸エステル、メタクリル酸エステル、アクリル酸、メタクリル酸、コロン酸、マレイン酸、イタコン酸、フマル酸、ビニルピロリドン、ビニルエーテル類等が挙げられ、このうちの2種以上を用いても良い。

【0075】一般式(L)中、xは10～70モル%、yは0～60モル%、zは0～70モル%を表す。但し

(C)を2種以上用いる場合、zはその合計のモル%を表す。

【0076】本発明に使用する水溶性カチオン性ポリマーと親水性バインダーは重量比で0.3:1～3:1であることが好ましく、特に好ましくは0.5:1～2:1である。この比率より水溶性カチオンポリマーの比率が小さいと色素の耐水性、耐湿が不十分であり、この比率より大きいとインクの吸収性がわるくなり、プリント画質が低下する。

【0077】本発明に使用する水溶性カチオン性ポリマーは支持体上に設けられた少なくとも2層のインク受容層のうち、少なくとも支持体から最も離れた側の層に含有されることが必要で、さらにこれ以外の層に含有しても構わない。支持体から最も離れた側の層に含有せず、支持体に近い側の層にのみ含有する場合、色素の耐水性が不十分で、好ましくない。

【0078】以下に本発明に使用するカチオン性ポリマーの具体例を示すが、これに限定されるものではない。

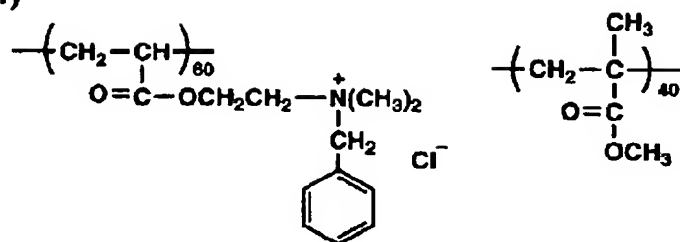
【0079】

【化3】

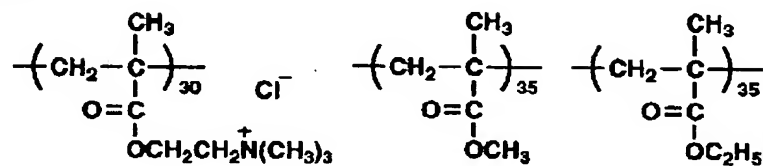
15

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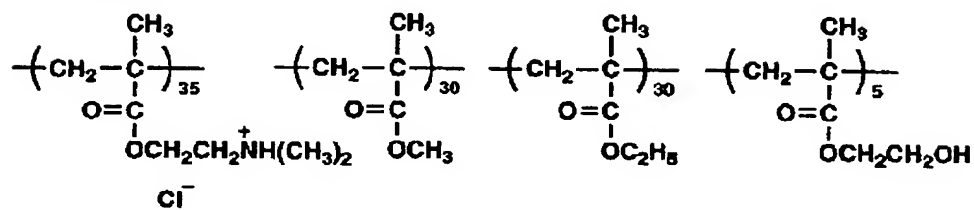
(C-1)



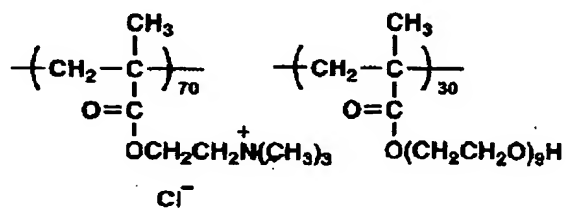
(C-2)



(C-3)



(C-4)



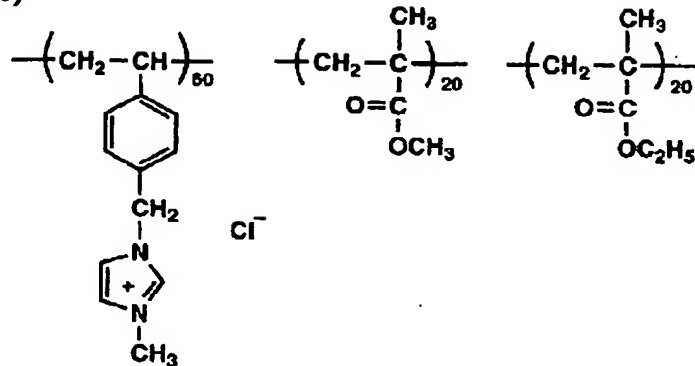
【0080】

【化4】

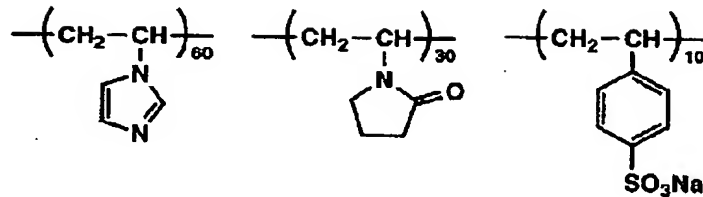
17

18

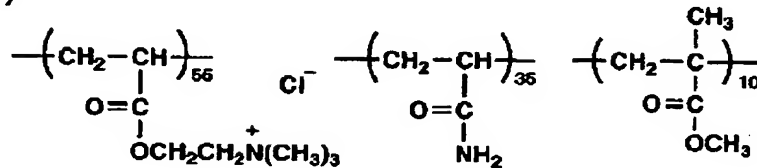
(C-5)



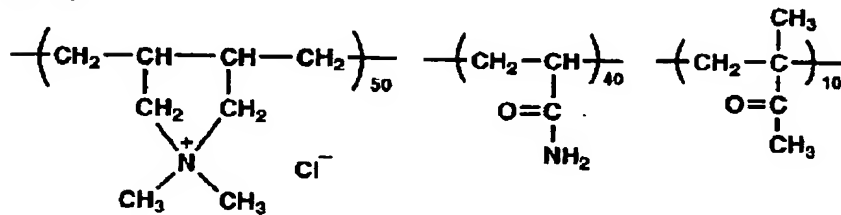
(C-6)



(C-7)



(C-8)



【0081】本発明のインクジェット記録用紙は、水溶性染料の耐光性を向上させる目的で退色防止剤として画像安定剤及び紫外線を吸収する化合物から選ばれる少なくとも1種を含有させることが好ましい。画像安定剤は水溶性のものを選択して塗布液に混合してもよいし、油溶性のものをオイル分散し油滴として塗布液に混合してもよい。

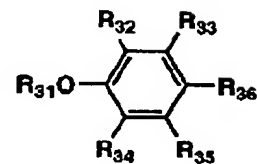
【0082】本発明に用いる画像安定剤は、例えば特開昭57-74192号、同57-87989号、同60-72785号、同61-146591号、特開平1-95091号、同3-13376号等に記載されている退色防止剤が挙げられる。

【0083】好ましい画像安定剤として、一般式(ST-I)及び(ST-II)で表される化合物が挙げられる。

【0084】

【化5】

一般式(ST-I)



【0085】式中、R₃₁は水素原子、アルキル基、アルケニル基又はアリール基を表し、R₃₂、R₃₃、R₃₄、R₃₅及びR₃₆は各々、水素原子、ハロゲン原子、シアノ基、ニトロ基、ヒドロキシル基、スルホ基又は1価の有機基を表す。

【0086】ただし、R₃₁が水素原子の場合、R₃₂及びR₃₄が同時に水素原子であることはない。又、R₃₁がアルキル基、アルケニル基又はアリール基である場合、R

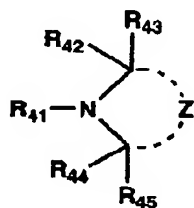
32、R₃₃、R₃₄、R₃₅及びR₃₆の少なくとも一つは、—OR₃₇（R₃₇はアルキル基又はアルケニル基）又は—N（R₃₈）R₃₉、（R₃₈及びR₃₉は各々、水素原子、アルキル基又はアルケニル基）である。

【0087】R₃₁とR₃₂、R₃₂とR₃₃、R₃₃とR₃₆、R₃₆とR₃₅、R₃₅とR₃₄、R₃₄とR₃₁は各々、互いに結合して環を形成してもよい。

【0088】

【化6】

一般式(ST-II)



【0089】式中、R₄₁は水素原子、アルキル基、アルケニル基、フェニル基、ヒドロキシル基、スルホニル基、スルフィニル基又はアシル基を表し、R₄₂、R₄₃、R₄₄及びR₄₅は各々、水素原子又はアルキル基を表す。Zは5～7員の含窒素複素環を形成するのに必要な非金属原子群を表す。

【0090】R₄₁とR₄₂、R₄₂とR₄₃、R₄₄とR₄₅、R₄₄とR₄₁は各々、互いに結合して環を形成してもよい。

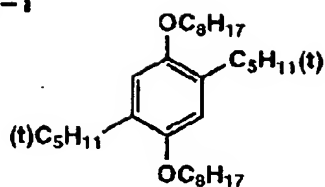
【0091】本発明に用いる特に好ましい画像安定剤の例を以下に示す。

【0092】

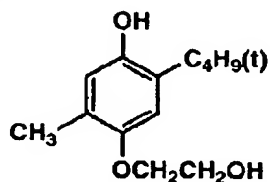
【化7】

21

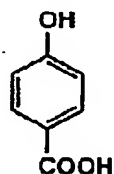
ST-1



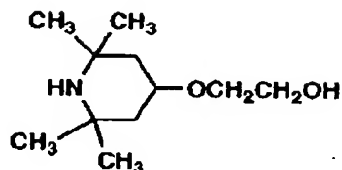
ST-3



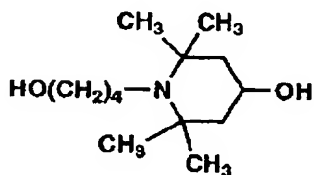
ST-5



ST-7

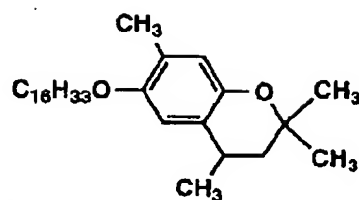


ST-8

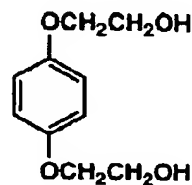


22

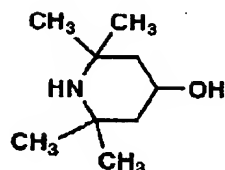
ST-2



ST-4



ST-6



【0093】本発明のインクジェット記録用紙は、水溶性染料の耐光性を向上させる目的で紫外線を吸収する化合物を含有させることができる。紫外線を吸収する化合物としては、例えば特開昭57-74193号、同57-87988号及び同62-261476号等に記載の紫外線吸収剤が挙げられる。媒染剤層に存在する水溶性染料に紫外線が到達しないようにするには、これらの紫外線吸収剤を媒染剤層よりも支持体から見て遠い層に含有させるのが効果的である。

【0094】上記、退色防止剤の使用量は0.01～5 g/m²が好ましく、0.1～2 g/m²が更に好ましい。

【0095】本発明のインクジェット記録用紙の任意の

インク受容性層中には、必要に応じて各種の添加剤を含有させることができる。例えばアニオン、カチオンまたはノニオン等の各種の公知の界面活性剤、特開昭59-42993号公報、同59-52689号公報、同62-280069号公報、同61-242871号公報および特開平4-219266号公報等に記載されている蛍光増白剤、硫酸、リン酸、クエン酸、水酸化ナトリウム、水酸化カリウム、炭酸カリウム等のpH調整剤、消泡剤、防腐剤、増粘剤、硬膜剤、帯電防止剤、マツト剤等の公知の各種添加剤を含有させることもできる。

【0096】高い空隙率の皮膜の脆弱性を劣化させずに得るために前記親水性バインダーが硬膜剤によって硬膜されていることが好ましい。硬膜剤は一般的には前記親

水性バインダーと反応しうる基を有する化合物あるいは親水性バインダーが有する異なる基同士を促進するような化合物であり、親水性バインダーの種類に応じて適宜選択して用いられる。硬膜剤の具体例としては、例えば、エポキシ系硬膜剤（ジグリシジルエチルエーテル、エチレングリコールジグリシジルエーテル、1, 4-ブタンジオールジグリシジルエーテル、1, 6-ジグリシジルシクロヘキサン、N, N-ジグリシジル-4-グリシジルオキシアニリン、ソルビトールポリグリシジルエーテル等）、アルデヒド系硬膜剤（ホルムアルデヒド、グリオキサール等）、活性ハロゲン系硬膜剤、

（2, 4-ジクロロ-4-ヒドロキシ-1, 3, 5-ス-トリアジン等）、活性ビニル系化合物（1, 3, 5-トリシアクリロイルヘキサヒドロ-ス-トリアジン、ビスビニルスルホンメチルエーテル等）、ほう酸及びその塩、ほう砂、アルミみょうばん等が挙げられる。

【0097】特に好ましい親水性バインダーとして、ポリビニルアルコール及びその誘導体を使用する場合には、ホウ酸及びその塩から選ばれる硬膜剤である。本発明でホウ酸またはその塩としては、ホウ素原子を中心原子とする酸素酸及びその塩のことを示し、具体的にはオルトホウ酸、二ホウ酸、メタホウ酸、四ホウ酸、五ホウ酸及び八ホウ酸及びそれらの塩が含まれる。

【0098】上記硬膜剤の使用量は親水性バインダーの種類、硬膜剤の種類、無機微粒子の種類、親水性バインダーに対する比率等で変化するが、概ね親水性バインダー1g当たり1~200mg、好ましくは5~100mgである。

【0099】上記硬膜剤は空隙層を構成する塗布液を塗布する際に空隙層形成の塗布液中及びまたは空隙層に隣接するその他の層を形成する塗布液中に添加しても良く、あるいは予め硬膜剤を含有する塗布液を塗布してある支持体上に前記空隙層を形成する塗布液を塗布したりさらには空隙層を形成する硬膜剤非含有の塗布液を塗布乾燥後に硬膜剤溶液をオーバーコートする等して空隙層に硬膜剤を供給することができるが、好ましくは製造上の効率から空隙層を形成する塗布液またはこれに隣接する層の塗布液中に硬膜剤を添加して空隙層を形成すると同時に硬膜剤を供給するのが好ましい。

【0100】本発明のインクジェット記録用紙のインク吸収層の皮膜の脆弱性を改良するために各種液滴を含有することが好ましいが、そのような油滴としては、室温での水に対する溶解性が約0.01重量%以下の疎水性高沸点有機溶媒（流動パラフィン、ジオクチルフタレート、トリクレジルホスフェート、シリコンオイル等）や重合体粒子（スチレン、ブチルアクリレート、ジビニルベンゼン、ブチルメタクリレート、ヒドロキシエチルメタクリレート等のモノマーを1種以上重合させた粒子）を含有させることができる。そのような油滴は、好ましくは親水性バインダーに対して10~50重量%用いる

ことができる。皮膜の脆弱性に対しては、分子量が300以下のポリオール類を含有することも好ましい。このようなポリオール類としては例えば、エチレングリコール、ジエチレングリコール、トリエチレングリコール、テトラエチレングリコール、ポリピレングリコール、グリセリン、1, 6-ヘキサジオール、1, 2-シクロヘキサジオール、分子量300以下のポリエチレングリコールあるいはポリエチレングリコール等が挙げられる。

10 【0101】本発明のインクジェット記録用紙の支持体としては、従来インクジェット用記録用紙として公知のものを適宜使用できる。

【0102】透明支持体としては、例えば、ポリエステル系樹脂、ジアセテート系樹脂、トリアセテート系樹脂、アクリル系樹脂、ポリカーボネート系樹脂、ポリ塩化ビニル系樹脂、ポリイミド系樹脂、セロハン、セルロイド等の材料からなるフィルムや板、およびガラス板などを挙げられ、この中でもOHPとして使用されたときの輻射熱に耐える性質のものが好ましく、ポリエチレンテレフタレートが特に好ましい。このような透明な支持体の厚さとしては、約10~200μmが好ましい。

20 【0103】また、透明である必要のない場合に用いる支持体としては、例えば、一般の紙、合成紙、樹脂被覆紙、布、木材、金属等からなるシートや板、および上記の透光性支持体を公知の手段により不透明化処理したもの等を挙げることができるが、基紙の少なくとも一方に白色顔料等を添加したポリオレフィン樹脂被覆層を有する樹脂被覆紙（いわゆるRCペーパー）、ポリエチレンテレフタレートに白色顔料を添加してなるいわゆるホワイトペットが好ましい。支持体とインク受像層の接着強度を大きくする等の目的で、インク受容層の塗布に先立って、支持体にコロナ放電処理や下引処理等を行うことが好ましい。さらに、本発明の記録用紙は必ずしも無色である必要はなく、着色された記録用紙であってもよい。

30 【0104】本発明の無機微粒子を含有する層を支持体上に塗布する方法は公知の方法から適宜選択して行うことができるが、ロールコート法、ロッドバーコート法、エアナイフコート法、スプレーコート法、カーテンコート法あるいは米国特許第2681294号記載のホッパーを使用するエクストルージョンコート法等が好ましく用いられる。

【0105】また、ゼラチンやゼラチン誘導体、κ-カラギーナン等の様なゾルゲル変換可能な親水性バインダーを用いる場合には、特開平6-64306号公報に記載されているように支持体上に塗布後、冷却してゲル状態にした後、コールドドライ法で乾燥する方法で行っても良い。

50 【0106】本発明のインクジェット記録用紙を用いて画像記録する際には、水性インクを用いた記録方法が用

いられる。

【0107】本発明で言う水性インクとは、下記着色剤及び液媒体、その他の添加剤から成る記録液体である。着色剤としてはインクジェットで公知の直接染料、酸性染料、塩基性染料、反応性染料あるいは食品用色素等の水溶性染料が使用できる。

【0108】水性インクの溶媒としては、水及び水溶性の各種有機溶剤、例えば、メチルアルコール、イソプロピルアルコール、*n*-ブチルアルコール、*tert*-ブチルアルコール、イソブチルアルコール等のアルコール類；ジメチルホルムアミド、ジメチルアセトアミド等のアミド類；アセトン、ジアセトンアルコール等のケトンまたはケトンアルコール類；テトラヒドロフラン、ジオキサン等のエーテル類；ポリエチレングリコール、ポリプロピレングリコール等のポリアルキレングリコール類；エチレングリコール、プロピレングリコール、ブチレングリコール、トリエチレングリコール、1, 2, 6-ヘキサントリオール、チオジグリコール、ヘキシレングリコール、ジエチレングリコール、グリセリン、トリエタノールアミン等の多価アルコール類；エチレングリコールメチルエーテル、ジエチレングリコールメチル（又はエチル）エーテル、トリエチレングリコールモノブチルエーテル等の多価アルコールの低級アルキルエーテル類等が挙げられる。

【0109】これらの多くの水溶性有機溶剤の中でも、ジエチレングリコール、トリエタノールアミンやグリセリン等の多価アルコール類、トリエチレングリコールモノブチルエーテルの多価アルコールの低級アルキルエーテル等は好ましいものである。

【0110】その他の水性インクの添加剤としては、例

〔塗布液-1〕

純水	1000ml
平均粒径約7nmの微粒子シリカ	150g
平均重合度3500のポリビニルアルコール（5%水溶液） （ケン化度89%）	500g
カチオン性ポリマー（表1に記載）	（表1に記載）
界面活性剤-3	1.2g
ホウ砂（4%水溶液）	20ml

上記液を高速ホモジナイザーで分散して白色半透明な塗布液を得た。

〔塗布液-2〕

純水	1000ml
平均粒径約7nmの微粒子シリカ	150g
平均重合度3500のポリビニルアルコール（5%水溶液） （ケン化度89%）	500g
カチオン性ポリマー（表1に記載）	（表1に記載）
界面活性剤-1	0.70g
界面活性剤-2	0.30g
ホウ砂（4%水溶液）	20ml

表面張力調整剤、湿潤剤、界面活性剤、及び防錆剤、等が挙げられる。

【0111】水性インク液は記録用紙に対する濡れ性を良好にするために、20℃において、25～60dyn/cm、好ましくは30～50dyn/cmの範囲内の表面張力を有するのが好ましい。

【0112】本発明のインクジェット記録用紙を用いて画像記録する際のインク吐出方式は、水性インクを吐出可能なインクジェット記録方式であればよく、例えば

「インクジェット記録技術動向」中村孝一編著（日本科学情報（株）、1995）p. 1～14に記載の連続噴射荷電制御方式やオンデマンド方式等の記録方式を用いることができる。しかし、これらの中でもオンデマンド方式の記録方式に適用して使用することにより、より大きな効果を得ることができる。

【0113】

【実施例】以下に本発明の実施例を挙げて説明するが、本発明はこれらの例に限定されるものではない。なお、実施例中で「%」は特に断りのない限り絶乾重量%を示し、添加量は各々インクジェット記録用紙1m²当たりの量を示す。

【0114】実施例1

100g/m²の原紙両面をポリエチレンで被覆した紙支持体（厚さ140μm、記録面側のポリエチレン層中に7重量%のアナターゼ型二酸化チタン含有。記録面の裏面側にバック層としてアルカリ処理ゼラチン1.2g/m²と硬膜剤を含有する層を有する）上の記録面側に、塗布液-1と、上層として塗布液-2を各々湿潤膜厚100μmで同時重層塗布乾燥を行い記録用紙1を得た。この皮膜の空隙容量は約25ml/m²であった。

【0115】

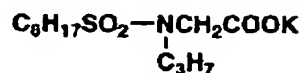
【0116】

上記で用いた化合物の構造を以下に示す。

【0117】

【化8】

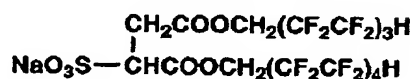
界面活性剤-1



界面活性剤-2



界面活性剤-3



【0118】上記液を高速ホモジナイザーで分散して白色半透明な塗布液を得た。

【0119】表1に示すように、使用するシリカの1次粒子径、水溶性カチオンポリマー、退色防止剤を添加、カチオンポリマーと全ポリビニルアルコールの重量比を変える他は記録用紙1と同様に、記録用紙2～19を作成した。できあがった記録用紙の乾燥膜厚と空隙容量も共に表1に示した。

【0120】

10 【表1】

20

記録用紙	第1層		第2層		全層	
	シリカ1次粒子径 (nm)	カチオン性ポリマー	カチオン性ポリマー	退色防止剤	カチオン性ポリマー/PVA (重量比)	空隙容量 ml/m ²
1 (本発明)	7	—	C-2	—	0.7	25.0
2 (本発明)	7	—	C-6	—	0.7	24.1
3 (本発明)	7	—	C-7	—	0.7	24.5
4 (本発明)	7	C-2*	C-2*	—	0.7	24.8
5 (本発明)	7	—	C-2	—	0.2	25.7
6 (本発明)	7	—	C-2	—	0.5	25.3
7 (本発明)	7	—	C-2	—	2	23.8
8 (本発明)	7	—	C-2	—	3	23.0
9 (本発明)	7	—	C-2	—	4	21.5
10 (本発明)	7	—	C-6	①	0.7	23.8
11 (本発明)	7	—	C-6	②	0.7	23.7
12 (本発明)	7	—	C-6	③	0.7	23.3
13 (本発明)	12	—	C-7	—	0.7	24.1
14 (本発明)	20	—	C-7	—	0.7	23.1
15 (比較例)	40	—	C-7	—	0.7	20.5
16 (本発明)	7	—	I	—	0.7	25.2
17 (比較例)	7	C-2	—	—	0.7	24.7
18 (比較例)	7	—	II	—	0.7	19.8
19 (比較例)	7	—	—	—	0.7	19.8

【0121】*：記録用紙4は、カチオン性ポリマーを第1層と第2層に等量に分けて添加した。

【0122】①：記録用紙10は、下記（分散物-1）を40ml添加した。

【0123】②：記録用紙11は、例示化合物ST-4を10g添加した。

【0124】③：記録用紙12は、例示化合物ST-5を10g添加した。

溶液1

紫外線吸収剤-1	1 g
ジ- <i>i</i> -デシルフタレート	1 g
酢酸エチル	5 ml

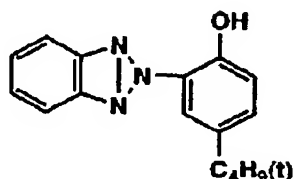
溶液2

ゼラチン	0.5 g
界面活性剤-4 (トリ- <i>i</i> -プロピルナフタレンスルホン酸ナトリウム)	0.2 g
純水	15 ml

上記で用いた化合物の構造を以下に示す。

【0127】

紫外線吸収剤-1



【0128】得られた各々のインクジェット記録用紙について、セイコーエプソン株式会社製インクジェットプリンターMJ-900Cを用い、評価パターンを印字し以下の項目の評価を行った。

【0129】(1) インク吸収性

イエローおよびシアンのそれぞれ最大インク量の30%になるように均一に吐出させて記録し、ベタ部の赤色反射濃度をマイクロデンストメーター（アパーチャ=200μmφ）を用いて20点測定し、その濃度のバラツキの標準偏差を求め平均反射濃度で割った値を求めた。

【0130】インク吸収性が良好な場合には画像にムラが無くこの値が小さくなるが、インク吸収性が低下するとこのお互いのインク液滴同士が記録紙上で互いにビーディングを起こしてムラになりこの値が増加する。

【0131】(2) 乾燥性

イエローとマゼンタの60%印字部を印字後5分後、記録用紙の裏面と重ね合わせ、120g/cm²の加重をかけて1分間放置、裏面へのインクの転写度合いを下記基準で目視評価した。

【0132】

◎：全く転写なし

○：僅かに転写するが、印字画像にはほとんど影響なし

×：多量のインクが転写、印字画像に影響大

(3) 耐水性

【0125】（分散物-1）下記組成の溶液1と溶液2を調製し、混合して超音波分散機にて分散した。

【0126】

【化9】

印字試料を20℃の水中に10分間浸せきした後、乾燥し、マゼンタの最高濃度部分の印字画像の耐水性を残存濃度で比較した。濃度の高いものから◎○△×の4段階で評価した。

【0133】(4) 耐湿性

印字後の試料を23℃、20%RHで2週間保存後、60℃80%RHで3日間保存し各色の滲み度合いを評価した。評価は

◎：全く滲みなし

○：滲み幅が約0.1mm未満（視覚的には滲みが僅かに認められる）

△：滲み幅が0.1mm～0.5mm未満（視覚的には許容不可）

×：0.5mm以上（画像として価値なし）

(5) 耐光性

マゼンタの最高濃度部分の試料をキセノンフェードメーターで20時間光照射し、照射後/照射前の反射濃度比をもとめた。

【0134】(6) 光沢度

印字面を日本電色工業株式会社製変角光沢度計（VGS-1001DP）を用いて60度光沢を測定した。

【0135】得られた結果を表2に示す。

【0136】

【表2】

記録用紙	インク吸収性	乾燥性	耐水性	耐湿性	耐光性	光沢度(%)
1 (本発明)	0.10	○	○	○	75	57
2 (本発明)	0.10	○	○	○	70	50
3 (本発明)	0.10	○	○	○	70	51
4 (本発明)	0.10	○	◎	◎	70	55
5 (本発明)	0.08	◎	△	△	80	65
6 (本発明)	0.09	○	○	○	75	60
7 (本発明)	0.12	○	◎	○	70	50
8 (本発明)	0.13	○	◎	○	65	47
9 (本発明)	0.14	△	◎	◎	65	40
10 (本発明)	0.10	○	○	○	90	50
11 (本発明)	0.10	○	○	○	92	51
12 (本発明)	0.10	○	○	○	95	50
13 (本発明)	0.10	○	○	○	75	51
14 (本発明)	0.11	○	○	○	70	47
15 (比較例)	0.18	△	○	○	70	29
16 (本発明)	0.10	○	△	○	70	49
17 (比較例)	0.10	○	△	×	80	60
18 (比較例)	0.17	△	○	△	60	52
19 (比較例)	0.09	◎	×	×	70	65

【0137】表2から、本発明のインクジェット記録用紙は良好なインク吸収性、乾燥性、耐水性、耐湿性、耐光性、光沢度を有していることがわかる。

【0138】1次粒径の大きいシリカを用いた記録用紙15は光沢性が大きく低下し、下層のみにカチオン性ポリマーを添加した記録用紙17、水溶性でないカチオンポリマーを添加した記録用紙18、カチオン性ポリマーを添加していない記録用紙19は耐水性、耐湿性が大きく低下する。

【0139】本実施例では不透明で光沢のある紙支持体を用いた場合について説明したが、透光性のある支持体を用いることでスライドやOHP等の光学機器により記録画像をスクリーン等への投影により観察するものや、カラー印刷のポジ版を作成する際の色分解版、あるいは

液晶等のカラーディスプレイに用いるCFM等の透過を利用する用途に好適なインクジェット記録用紙を提供することができる。

【0140】また、本発明の記録シートについて、主にインクジェット方式に用いる場合を説明してきたが、インクジェット方式以外にも水性インクを利用する各種筆記用具やペンプロッター等の記録機器による記録に好適に利用できる。

【0141】

【発明の効果】以上、本発明のインクジェット記録用紙の構成を用いれば、水性インクによる印字において、高い光沢性を維持しつつしかも良好なインク吸収性が達成出来、かつ耐水性、耐湿性、耐光性が良好な高品位の画像を形成記録することが出来る。